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ELEMENTS OF CHEMISTRY:

THEORETICAL AND PRACTICAL.

ELEMENTS OF CHEMISTRY:

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PART II.

INORGANIC CHEMISTRY.

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PREFACE

TO

THE SIXTH EDITION.

The order in which the non-metallic elements and their compounds are described is the same in this Edition as in the last, commencing with the elements which form the least complex compounds, and gradually passing to those which form more numerous and complicated substances; for the same reason seven typical elements, and their compounds with one another, are first studied before dealing with those of which they may be regarded as representatives.

Hydrogen, as the standard of reference for the atomic weights of the elements and for the densities of gases, besides being employed as the measure of the atomicity of the other elements, occupies the first place, as the type of electro-positive substances. It is followed by chlorine as a specimen of an electro-negative element, remarkable for its chemical activity, and one which forms a large and important series of combinations. The compound of this element with hydrogen forms the subject of the next section. Oxygen is then brought before the notice of the student as one of the most important elements, and on that account is, even now, very often placed first in order, as was the case in the earlier editions of this work; being a dyad, however, it does not produce such simple combinations as those of chlorine. The compounds of oxygen with hydrogen and with chlorine and hydrogen are next described. Then follow boron, a triad; carbon, a tetrad; nitrogen, a pentad; sulphur, a hexad;

and the compounds they produce with the elements previously studied. The remaining non-metals are described in an order consistent with that employed in the case of the typical ones.

The whole work has been carefully revised, and many additions made, especially in the non-metallic compounds; the metallurgy of iron, also, which is one of the most important of our technical industries, has been treated as fully as was consistent with the character of this work, and sections on the recently discovered metals, Gallium and Davyum, have been introduced.

The formulæ remain substantially the same as in the last edition; the constitutional formulæ suggested by Dr. Frankland, which are occasionally introduced, being inclosed in square brackets, so as to indicate clearly that they are an interpolation into the original work, although they are not inconsistent with the ideas developed in the earlier editions.

It is to be hoped that the slight typographical alteration of printing the side headings of the paragraphs in bolder type, will facilitate the use of the book by the student, and also that the large number of references introduced, particularly to the more recent researches, will be found useful by those who desire more detailed information than could be given in an elementary work like the present. The Index has been made as complete as possible; and, as in Part I. of this Edition, the dates of references have been introduced in almost every instance.

In conclusion, the Editor desires to express his sincere thanks to Mr. Frederick Sear for his valuable assistance in reading the proofs; for by his skill and care the number of errors unavoidable in a work of this kind has been materially reduced.

SOMERSET HOUSE TERRACE, W.C.,
June, 1878.

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Symbols and Atomic Weights of the Elements as used in this Volume.

Names of Elements.	Symbol.	At. wt.	Names of Elements.	Symbol.	At. wt.
Aluminium	Al	27·5	Mercury	Hg	200
Antimony	Sb	122	Molybdenum	Mo	96
Arsenicum	As	75	Nickel	Ni	59
Barium	Ba	137	Niobium	Nb	94
Bismuth	Bi	210	Nitrogen	N	14
Boron	B	11	Osmium	Os	199
Bromine	Br	80	Oxygen	O	16
Cadmium	Cd	112	Palladium	Pd	106·5
Cæsium	Cs	132·6	Phosphorus	P	31
Calcium	Ca	40	Platinum	Pt	197·1
Carbon	C	12	Potassium	K	39·1
Cerium	Ce	141·3	Rhodium	Ro	104·3
Chlorine	Cl	35·5	Rubidium	Rb	85·5
Chromium	Cr	52·5	Ruthenium	Ru	104·2
Cobalt	Co	59	Selenium	Se	79·1
Copper	Cu	63·4	Silicon	Si	28
Davyum	Da	154 (?)	Silver	Ag	108
Didymium	Di	142·5	Sodium	Na	23
Erbium	E	113·7	Strontium	Sr	87·6
Fluorine	F	19	Sulphur	S	32
Gallium	Ga	69·9	Tantalum	Ta	182
Glucinum	G	9·3	Tellurium	Te	129
Gold	Au	196·6	Thallium	Tl	203·6
Hydrogen	H	1	Thorinum	Th	234
Indium	In	113·4	Tin	Sn	118
Iodine	I	127	Titanium	Ti	50
Iridium	Ir	198	Tungsten	W	184
Iron	Fe	56	Uranium	U	120
Lanthanum	La	140·4	Vanadium	V	51·3
Lead	Pb	207	Yttrium	Y	59·7
Lithium	L	7	Zinc	Zn	65
Magnesium	Mg	24	Zirconium	Zr	89·5
Manganese	Mn	55			

PART II.

INORGANIC CHEMISTRY.

CHAPTER I.

NOMENCLATURE—CLASSIFICATION OF THE ELEMENTS.

(331) The division of chemistry into inorganic and organic is purely artificial. The same laws which regulate the formation and decomposition of inorganic bodies prevail also in the case of organic compounds, and the properties of the bodies and their origin often make it extremely difficult to decide to which division they should be considered to belong. It is, however, convenient in many cases to retain the distinction, and perhaps the most accurate definition of organic chemistry is that given by Schorlemmer (*Jour. Chem. Soc.*, 1872, xxv. 428)—viz., "the chemistry of the Hydrocarbons and their derivatives." The student will be able fully to appreciate the signification of this definition when he studies the compounds which carbon produces with other elements.

Principles of Chemical Nomenclature.—Before proceeding to a description of the chemical properties of the different elementary substances, and of the compounds which are the result of their union with each other, it will be needful to explain the principles upon which the nomenclature in use amongst chemists has been founded. The object of the inventors of this language was, not merely to give a distinguishing name to the substances spoken of, but also to convey a knowledge of their components, and even of the proportions in which those components occur. In the less complicated substances with which the chemist has to deal, this object is very completely attained. In those of a more complex nature, the employment of symbols (13) becomes necessary, in order that the composition of the body may be fully indicated; and the *formula* of a substance, especially if it be derived from the animal or the vegetable kingdom, becomes an indispensable supplement to its name.

(332) **Elements.**—In the case of the elementary bodies, the common name of each is usually that by which it is distinguished in chemical language, if the substance—as is the case with many of the metals, such as lead, iron, copper, or zinc—be one which is familiarly known: if it be a body which the researches of the chemist have brought to light, the name is generally indicative of some marked peculiarity by which the element is characterized. Phosphorus, for example, is so named (from φῶς φορὸς, light bearing) because when exposed to the air it emits a feeble light which is visible in a darkened room; iodine derives its name from ἰοειδής (violet), in reference to the violet colour of its vapour; hydrogen (water producer, from ὕδωρ, γεννάω) is so called from the circumstance that it is a necessary component of water; and so on.

The attempt to introduce a strictly systematic nomenclature for the elementary substances has failed, owing to the strong hold which the popular names of those in familiar use have retained upon the language; but in the case of the metals more recently discovered a common termination in *um* has been assigned to them: as, for example, palladium, iridium, osmium, potassium, sodium, aluminium, &c. Among the non-metallic elements analogies are also pointed out by a similarity in the termination of the name: for instance, chlorine, iodine, bromine, and fluorine, have similar properties; and the existence of a certain analogy between carbon and silicon is indicated by the common termination of both.

(333) **Binary Compounds.**—When elements combine with each other to form a binary compound—that is to say, a compound in which two elements only are present, and in which also one atomatic proportion* only of each substance is

* We have already called attention (12*a*, 14) to the loose way in which the terms *atom*, *molecule*, and *equivalent* are often employed by chemists, and have pointed out the essential difference between the signification of the two terms. For example, an acid like the citric ($H_3C_6H_5O_7$), will require three times as much potassium to form with it a neutral salt, as is required by another acid, such as the nitric (HNO_3). The proportion of citric acid represented by the formula $H_3C_6H_5O_7$ is nevertheless sometimes inaccurately termed its *equivalent*, and the same term is also applied to the proportion of nitric acid represented by the formula HNO_3; yet it is manifest that these quantities of the two acids are not equivalent to each other, inasmuch as one of them neutralizes three times as much potassium as the other.

In order, therefore, to avoid this solecism, and at the same time to secure brevity in our descriptions, it will be convenient to speak of the relative quantities of each acid above cited as a *molecule* of their respective acids; a term warranted by the fact that the formula of each represents the simplest expression in symbols which can be adopted to indicate the smallest particle of the compound which can exist either in combination or in separate form.

concerned—the nature of both the components is specified by the name employed: for instance, a combination of oxygen with zinc is designated oxide of zinc or zincic oxide. The following table will illustrate the manner in which such modifications are applied; the symbols of the different compounds are given in the fifth column. It is to be observed that in employing symbols the symbol of the basylous or electro-positive element (261) is usually placed first.

The compounds of	are termed	For example:—		Or in symbols.
Oxygen	Oxides	Zincic oxide, or	Oxide of zinc	ZnO
Chlorine	Chlorides	Argentic chloride	Chloride of silver	AgCl
Bromine	Bromides	Sodic bromide	Bromide of sodium	NaBr
Iodine	Iodides	Potassic iodide	Iodide of potassium	KI
Fluorine	Fluorides	Potassic fluoride	Fluoride of potassium	KF
Nitrogen	Nitrides	Boric nitride	Nitride of boron	BN
Carbon	Carbides or Carburets	Nitric carbide (cyanogen)	Carbide of nitrogen	CN
Sulphur	Sulphides or Sulphurets	Cupric sulphide	Sulphide of copper	CuS
		Plumbic sulphide	Sulphuret of lead	PbS
Selenium	Selenides or Seleniurets	Mercuric selenide	Selenide of mercury	HgSe
		Cadmic selenide	Seleniuret of cadmium	CdSe
Phosphorus	Phosphides or Phosphurets	Calcic phosphide	Phosphuret of calcium	CaP

(334) **Multiple Compounds.**—It often happens, however, in consequence of the operation of the law of multiple proportions (10), that the same pair of elements forms two or more compounds endowed with different properties, and which contain different proportions of their components: the electro-negative element in this case is usually the one in which the multiple relation is observed; and the number of atoms in which it enters into combination in the particular case is indicated by prefixing to the name an abbreviation of the corresponding Greek ordinal; πρῶτος first, δεύτερος second, τρίτος third, &c. For example, there are four different oxides of osmium.

The first or lowest oxide	is termed	the osmium protoxide, or protoxide of osmium	OsO
The second oxide	„	osmium dioxide, or deutoxide of osmium . .	OsO_2
The third oxide	„	osmium trioxide, or tritoxide of osmium .	OsO_3
The fourth oxide	„	osmium tetroxide, or tessaroxide, or peroxide of osmium . . .	OsO_4

Sometimes the Latin prefixes are substituted for those derived from the Greek: thus the terms *bin*oxide and *deut*oxide of tin are used indifferently for a combination of one atom of tin and two atoms of oxygen, SnO_2. In the same way *ter*chloride of

antimony, $SbCl_3$, is used as synonymous with antimony *tri*chloride. The more complicated relation of 3 atoms to 2, or 1½ to 1 is expressed by the Latin prefix *sesqui*, which means 'one and a half.' For example, we speak of *sesqui*sulphide of iron, Fe_2S_3, and chromium *sesqui*oxide, Cr_2O_3. The highest oxide, chloride, or sulphide, is frequently termed the *per*oxide, *per*chloride, or *per*sulphide. For example, the compound $SbCl_5$ is termed either antimony pentachloride or perchloride of antimony, and CaS_5 is termed indifferently calcic persulphide or pentasulphide of calcium. This practice of using indifferently a Greek or a Latin prefix in the names of compounds belonging to the same series is etymologically reprehensible. If, for instance, the compound of tin, SnS, be termed the *protosulphide*, the compound, SnS_2, should, in order to preserve consistency, be termed the *deutosulphide* or *disulphide*, though in this case the use of the name *bisulphide* is sanctioned by custom.

(335) **Acids.**—If the oxides, when combined with the elements of water, possess acid characters, as, for example, is the case with some of the higher oxides of nitrogen, a different plan is adopted to mark this important peculiarity. At the time that the nomenclature was devised by Lavoisier and his coadjutors, oxygen was considered to be the element upon which the existence of the acid character mainly depended, as indeed its name (signifying generator of acids) implies. The system of nomenclature was therefore specially adapted to this idea. It frequently happens that an element forms more than one acid with oxygen: the compound which contains the largest proportion of oxygen is in this case indicated by making the name terminate in the syllable *ic*. Nit*ric* acid, HNO_3, for instance, is the acid of nitrogen in which the largest quantity of oxygen is found: in like manner sulphur*ic* acid, H_2SO_4, is the most highly oxidized acid of sulphur. A second acid which contains the same elements united with a smaller proportion of oxygen receives the name which ends with the syllable *ous*: thus nitr*ous* acid, HNO_2, and sulphur*ous* acid, H_2SO_3, indicate acids in which a smaller proportion of oxygen is present than in nitric and sulphuric acids. In a few cases an acid has been discovered which contains still more oxygen than the one to which the termination *ic* had been already appropriated. Chloric acid, for example, is represented as $HClO_3$, but an acid was subsequently found to exist, which has the composition $HClO_4$; in this case the prefix *per* (which is an abbreviation for ὑπέρ, or *super*, above) is employed, and the new compound has been termed *per*chloric

acid.* When an acid is known in which the proportion of oxygen is smaller than that which exists in the compound to which the termination *ous* has been appropriated, the prefix *hypo* (from ὑπό, below) is usually employed—for instance, chlorous acid consists of $HClO_2$, whilst the compound HClO, with a still smaller amount of oxygen is known as *hypo*chlorous acid.

The progress of research, however, has revealed other acids in which oxygen is wanting, but which are compounds of hydrogen. These acids are usually distinguished by prefixing the word *hydro*, as an abbreviation for hydrogen: for instance, chlorine and hydrogen form an acid HCl, *hydro*chloric acid, technically called muriatic acid: sulphur and hydrogen form H_2S, *hydro*sulphuric acid: cyanogen and hydrogen form HCy, *hydro*cyanic or prussic acid, and so on. Some writers, following the example of Thénard, transpose these terms: they speak of *chlorhydric* acid, *sulphydric* acid, and *cyanhydric* acid.

(336) **Salts.**—Owing to the change which has recently taken place in the views prevalent respecting the atomic constitution of chemical compounds, a great deal of confusion unfortunately exists at the present moment in the nomenclature adopted by different authors. This is nowhere more conspicuous than in the differences which prevail in the mode of designating the different varieties of salts.

At the time that our nomenclature was originally devised, it was supposed that a salt consisted of a combination of an acid with a basic oxide, and the name given to each salt was framed upon this idea; *sulphate of potash*, for example, indicated the salt formed by the combination of sulphuric acid with the alkaline base potash; *nitrate of soda*, the salt obtained by neutralizing nitric acid with soda. If the base has no single distinguishing name, as occurs with most of the insoluble oxides, a longer name was requisite. When, for instance, acetic acid acts upon oxide of copper, or formic acid upon oxide of lead, the salts

* The term acid has been employed by chemical writers up to a late period, to designate indifferently either the anhydrous bodies formed by the union of oxygen with the non-metallic elements, such as CO_2 and SO_3 (now commonly termed *anhydrides*, or bodies destitute of hydrogen), or the hydrated compounds produced by the action of water upon the anhydrides, such as H_2SO_4, oil of vitriol or sulphuric acid. To avoid this confusion, produced by the application of the same term to two substances essentially distinct, we shall limit the term acid to those hydrated bodies which are really salts of hydrogen: sulphuric acid, H_2SO_4, is then dihydric sulphate, or sulphate of hydrogen; nitric acid, HNO_3, is hydric nitrate, or nitrate of hydrogen; acetic acid, $HC_2H_3O_2$, hydric acetate, or acetate of hydrogen, and so on.

produced were named, in accordance with the principle just explained, *acetate of oxide of copper,* and *formate of oxide of lead;* but these long names became almost immediately shortened into *acetate of copper,* and *formate of lead;* terms which are obviously inconsistent with the names given to the salts of the alkalies and of the earths.

Many chemists have sought to remedy this inconsistency by introducing in every instance the name of the basyl or the metal into the salt, instead of that of the base or metallic oxide. They speak therefore of *sulphate of potassium,* and *nitrate of sodium,* as well as of *acetate of copper* and *formate of lead.*

Some writers, however, prefer, whilst still employing the name of the metal or basyl, to place it first in naming the salt, omitting the word *of* altogether; so that they speak of *potassium sulphate, sodium nitrate, copper acetate,* and *lead formate.*

Lastly, Berzelius, for reasons to be explained immediately, not only employs the name of the metal, but modifies its termination; so that he speaks of *potassic sulphate, sodic nitrate, cupric acetate,* and *plumbic formate.*

It is this last modification which will generally be adopted in this work; although cases will occasionally occur in which the other forms of nomenclature will be employed, for the sake of convenience.

From what has been just stated, it will be seen that four different usages are more or less prevalent in naming salts; these may be contrasted and compared together as in the following table:

K_2SO_4	Sulphate of potash,	Sulphate of potassium,
	Dipotassic sulphate,	Potassium sulphate.
$NaNO_3$	Nitrate of soda,	Nitrate of sodium,
	Sodic nitrate,	Sodium nitrate.
$Cu2C_2H_3O_2$	Acetate of oxide of copper,	Acetate of copper,
	Cupric diacetate,	Copper acetate.
$Pb2CHO_2$	Formate of oxide of lead,	Formate of lead,
	Plumbic diformate,	Lead formate.

When the acids by their action upon bases form salts, the degree of oxidation in the acid is still indicated by the name of the salt. When acids ending in *ic* form salts, in naming such compounds the termination of the acid is changed into *ate*: thus the salt formed by the action of nitr*ic* acid upon lime is termed calcic nitr*ate,* or more strictly, calcic dinitrate, Ca_2NO_3. When sulphur*ic* acid acts upon protoxide of iron, the salt pro-

duced is called sulph*ate* of iron, or ferrous sulph*ate*, $FeSO_4$: perchloric acid by its action upon potassic hydrate furnishes the salt called potassic perchlor*ate*, $KClO_4$. If the name of the acid end in *ous*, the termination is changed to *ite* in naming the salt; for example, sulphur*ous* acid and baryta by their mutual action form a salt called baric sulph*ite*, $BaSO_3$: hypochlor*ous* acid and soda by their mutual action form sodic hypochlor*ite*, NaClO.

It may here be well to caution those who are just commencing the study of chemistry, of the necessity of distinguishing clearly between compounds such as the sulph*ites* and the sulph*ates*, or the sulph*ides* and the sulph*ites*. Disodic sulphide, Na_2S, for example, is a compound, containing a product of the direct combination of two elementary substances, whereas disodic sulphite, Na_2SO_3, is a more complex compound formed by the action of two compound bodies upon each other. Disodic sulphate, Na_2SO_4, again, contains one proportional more of oxygen than disodic sulphite.

If more than one equivalent of the oxion (or radicle of an acid) be united with one equivalent of a metal, there is no difficulty in pointing out this fact in the name. A compound of two equivalents of sulphion $(SO_4)''$ and two of potassium (K_2) would be spoken of as dipotassic sulphate, or sulphate of potassium, K_2SO_4; but there is another compound of potassium with sulphuric acid, in which two equivalents of the dyad oxion are present and only one equivalent of the metal; this compound, $KHSO_4$, is known as the bisulphate of potash, or more correctly, as hydric potassic sulphate, or sulphate of potassium and hydrogen, the atom of hydrogen taking the place of the second equivalent of the metal; the circumstance of the additional equivalent of acid in this and in other analagous cases being still often conveniently indicated by the prefix *bi* (from the Latin *bis*, twice) or *di* (from the Greek δίς), which is made to precede the name of the acid contained in the neutral salt.

Generally speaking, a metal forms only one basic oxide—that is to say, only one oxide which has the power of forming salts by interaction with acids; but there are several exceptions to this rule. Iron, for example, may form salts corresponding to the protoxide, FeO. Such salts were formerly distinguished as *protosalts*: $FeSO_4.H_2O+6OH_2$, represents the composition of the crystallized sulphate of protoxide of iron, often described as protosulphate of iron; but there is another series of salts of iron derived from the peroxide or sesquioxide, Fe_2O_3, of the metal; these were distinguished as the *persalts*, or *sesquisalts* of iron:

$Fe_2O_3.3SO_3$, or Fe_23SO_4, represents the sulphate of the peroxide or sesquioxide of iron, and it is frequently termed the persulphate, or sesquisulphate of iron. These terms, although still used, are not free from ambiguity. Berzelius preferred to call the protoxide of iron, *ferrous* oxide, and the protosulphate, *ferrous* sulphate, whilst the sesquioxide he termed *ferric* oxide, and the sesquisulphate was upon his plan called *ferric* sulphate. This form of nomenclature unites brevity with precision, and will usually be employed in this work.

Many of these systematic names have an uncouth aspect, and are often long and inharmonious, so that they are frequently abbreviated when the compound spoken of is one of constant recurrence. For example, the sulphates of the alkaline and earthy metals would receive systematic names such as the following:

K_2SO_4, dipotassic sulphate.
$KHSO_4$, hydric potassic sulphate.
Na_2SO_4, disodic sulphate.
$CaSO_4$, calcic sulphate.

It is, however, customary to speak of the normal or neutral salt of any acid without the numerical prefix; so that, for instance, K_2SO_4 is simply called potassic sulphate, and Na_2SO_4, sodic sulphate, though in reality these names do not indicate their atomic difference from the normal salt of a dyad like calcium, the sulphate of which, $CaSO_4$, is both commonly and correctly spoken of as calcic sulphate.

Again, in the case of the nitrates of the dyad metals, the salts are strictly dinitrates, nitrion $(NO_3)'$ being a monad; for example,

$Ca2NO_3$, calcic dinitrate.
$Ba2NO_3$, baric dinitrate.

Yet we commonly speak of them as calcic nitrate and baric nitrate, and do not in the name indicate the presence of two proportions of nitrion; whilst in the sodic salt $NaNO_3$, which is correctly spoken of as sodic nitrate, only one of nitrion is present. Again, in the ordinary or tribasic phosphates, the common lime phosphate, Ca_32PO_4, should be designated as tricalcic diphosphate, though usually this is abbreviated to calcic phosphate.

When, however, there are many salts of varying composition formed from the same acid, a strict adherence to system is often not only useful, but necessary, to avoid confusion. For example, in the three phosphates of soda formed from the ordinary tri-

basic acid, the proportions of the different basyls require indication:

H_3PO_4, trihydric phosphate.
Na_3PO_4, trisodic phosphate.
HNa_2PO_4, hydric disodic phosphate.
H_2NaPO_4, sodic dihydric phosphate.

Again, it may sometimes be useful to speak of Ca_32PO_4 as tricalcic diphosphate; of CaH_42PO_4 (superphosphate of lime) as calcic tetrahydric diphosphate; and of $HNaNH_4PO_4$ (microcosmic salt), as ammonic hydric sodic phosphate.

By prefixing the numeral in the name to the particular constituent in the salt, whether it be the hydrogen, the sodium, or the oxion, we indicate the number of proportions of the particular component which it precedes.

Other forms of nomenclature are applied in particular cases, but these will be best explained as the examples to which they refer arise.

(337) **Empirical and Rational Formulæ.**—In expressing the composition of a body by the use of symbols, the chemist may either content himself with simply stating the result of analysis by a mere enumeration of the elements and the relative number of proportionals of each, in which case he gives what is termed the *empirical formula* of the body; or he may give the numbers and relative proportions of the atoms present in one molecule of the compound, thus showing the *rational formula*, which, in mineral substances, is frequently the same as the empirical formula; or, lastly, he may attempt an explanation of the mode in which he conceives those elements to be associated together, and by the arrangement of his symbols may give expression to a theory of the constitution of the body, and thus assign to it a *constitutional formula*. A body can have but one empirical and one rational formula, but it may be represented by a variety of constitutional formulæ, according to the different views which may be taken as to the mode in which its components are arranged.

Crystallized magnesic sulphate, for example, has the following empirical formula:

(1) $MgH_{14}SO_{11}$;

that is to say, its constituents are present in the ratio of 1 atom of magnesium, 14 of hydrogen, 1 of sulphur, and 11 of oxygen. It is, however, never so written. The water which it contains

may be entirely driven off by a heat a little above 200° (392° F.): and the salt is often represented as consisting of magnesia, sulphuric anhydride, and water, as these are the materials out of which it may be formed: thus

$$(2)\ MgO.SO_3.7OH_2.$$

But it is found that at a heat of 100° (212° F.) 6 molecules of the water may be expelled, whilst the seventh molecule requires a much higher temperature, so that it appears to occupy a position in the salt different from that of the other 6: this fact may be indicated by slightly altering the second formula, as follows:

$$(3)\ MgO.SO_3.OH_2.6OH_2.$$

Many chemists, however, guided partly by the results of the electrolysis of the salt, suppose that when once an acid and a base have reacted on each other, their elements are arranged in an order different from that in which they existed when separate, and they prefer to represent the salt accordingly, as

$$(4)\ Mg.SO_4.OH_2.6OH_2;$$

or we may suppose that the oxygen atoms in the salt are differently placed, two being combined with the sulphur, and two being occupied in linking together the sulphur and magnesium, forming an atomic combination; the seven molecules of water present being merely united to the salt by a looser kind of attraction, producing what is sometimes called a molecular combination:

$$(5)\ SO_2(O_2Mg).7OH_2;$$

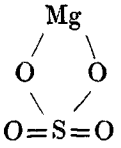
or, finally, the different condition in which one of these water molecules is placed may justify the conclusion that it is intimately combined with the salt, the two atoms of hydrogen being present in the compound in the form of hydroxyl, thus,

$$(6)\ SO(OH)_2(O_2Mg).6OH_2.$$

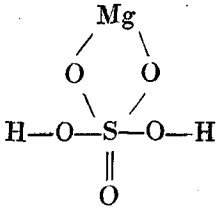
Each of the last five formulæ is a constitutional formula for magnesic sulphate; and each conveys far more information than the formula No. 1. Each represents a theory founded upon particular modes of decomposition which the salt may be made to experience.

It is impossible that all these formulæ should truly indicate

the molecular constitution of the salt, although each may represent the grouping of its component elements under particular circumstances. Constitutional formulæ are indeed indispensable as the exponents of the theories which guide the chemist in his researches, or which aid him in arranging and interpreting phenomena; but, like the theories that they embody, they are only temporary expedients, and they must consequently always be regarded as such, and must be modified or discarded when they no longer faithfully represent the conditions of our knowledge of the compounds which they are employed to indicate. The last two formulæ above given are the symbolic representations of what may be called the graphic or pictorial formulæ. The value of this kind of formula is not so apparent in mineral chemistry as in organic, in fact, in this latter it is almost indispensable, and is adopted, in principle at least, by a large number of chemists. Anhydrous magnesic sulphate graphically represented would be



and the hydrate with one molecule of water



In these formulæ the MgO_2 appears as a compound dyad radical directly united to the sulphur, and as radicals of this kind frequently occur, special symbols have been devised to represent them, thus the radical in question may be written Mgo″ and may be dignified by the special name *magnesoxyl*, being an analogue of *hydroxyl* HO or Ho. The thick initial letter, as already explained (16 *a*), indicates that all atoms and compound radicals following are directly combined with it, so that the two foregoing graphic formulæ may be written symbolically

$$SO_2(O_2Mg)'' \quad \text{or} \quad SO_2Mgo''$$
$$\text{and} \quad SO(OH)_2(O_2Mg)'' \text{ or } SOHo_2Mgo''.$$

The differences between empirical, rational, and constitutional formulæ may be well illustrated by those of acetic acid. The simplest formula obtained by analysis is CH_2O—the empirical formula. The molecule contains $C_2H_4O_2$—the rational formula. Three of the atoms of hydrogen appear to be differently placed from the fourth, three being directly combined to one of the carbon atoms, the other being linked by oxygen to the second carbon atom; whilst the carbon atoms are directly united; the constitutional formula will therefore be $CH_3.COOH$ or

$$\begin{cases} CH_3 \\ CO(OH) \end{cases} \quad \text{or} \quad \begin{cases} CH_3 \\ COHo \end{cases}$$

In these two formulæ the brace indicates direct union between the elements, the symbols of which are placed next to it.

(338) **General Arrangement of the Elements adopted in this Work.**—The general division of the elementary bodies into non-metallic and metallic has been already pointed out. There is, however, no strict line of demarcation between the non-metallic and the metallic elements.

The bodies which are considered as non-metallic constitute the electro-negative ingredient in the binary combinations which they form with the metals, and are most of them insulators of the voltaic current. Carbon and silicon, however, in certain forms, act as conductors of electricity. The compounds of the non-metals with oxygen generally show but little tendency to unite with acids; on the contrary, the higher oxides of most of them form compounds which, if acted on by water, furnish powerful acids. These acid forming oxides, except silica, are readily soluble in water; and even silica, under certain circumstances, may be obtained in solution.

The metals, on the other hand, are characterized by a certain combination of opacity and compactness, which gives them, when polished, a peculiar brilliancy, termed the metallic lustre; they are good conductors of heat and electricity, and most of them, by combination with oxygen, form powerful bases. It is sometimes difficult, however, to determine whether a body should be regarded as a metal or not. Arsenicum has a high metallic lustre; but it is more closely allied to phosphorus than to any other elementary substance, and both its oxides, when dissolved in water, are endowed with well-marked acid properties. Tellurium also exhibits the closest analogy with selenium and with sulphur, but it possesses high lustre, and some conducting power for electricity.

The subdivision of the simple substances into non-metallic and metallic is, however, convenient to the student, and it will therefore be retained in this work. The order in which the different elementary bodies will be treated is not in all cases that which a rigid adherence to analogy would indicate, although analogy has guided us, excepting in those instances in which it seemed more advantageous to the student to follow a different course. In most cases we shall first examine the chemical properties which are exhibited by each of the elements in its uncombined form; we shall then study the general nature of its actions upon other elements, and shall afterwards examine the more important compounds into the formation of which it enters.

In describing the properties of the elementary bodies, it will be found a convenient arrangement to consider, in the first place, hydrogen, chlorine, oxygen, boron, carbon, nitrogen, and sulphur as typical of all the rest, since a complete study of these elements and of the compounds they form with one another will much facilitate the further consideration of the groups which they represent.

For the convenience of description and of reference, the metals will be arranged in eight groups, in the following order. The elements which compose each group generally present some natural resemblance, though, as already stated, the classification does not in all cases bring together those which, in chemical habitudes, are really the most closely allied.

I. *Alkali-Metals—5 in number.*

1. Potassium.	3. Lithium.	5. Rubidium.
2. Sodium.	4. Cæsium.	

II. *Alkaline Earth-Metals—3 in number.*

1. Barium.	2. Strontium.	3. Calcium.

III. *Earth-Metals—9 in number.*

1. Aluminium.	4. Yttrium.	7. Cerium.
2. Gallium.	5. Erbium.	8. Lanthanum.
3. Glucinum.	6. Terbium.	9. Didymium.

IV. *Magnesian Metals—3 in number.*

1. Magnesium.	2. Zinc.	3. Cadmium.

V. *Metals more or less analogous to Iron—6 in number.*

1. Cobalt.	3. Uranium.	5. Chromium.
2. Nickel.	4. Iron.	6. Manganese.

VI. *Metals which yield Acids*—12 *in number.*

1. Tin.	5. Molybdenum.	9. Vanadium.
2. Titanium.	6. Tungsten.	10. Arsenicum.
3. Zirconium.	7. Niobium.	11. Antimony.
4. Thorinum.	8. Tantalum.	12. Bismuth.

VII. 4 *Metals.*

1. Copper.	2. Lead.	3. Thallium.	4. Indium.

VIII. *Noble Metals*—9 *in number.*

1. Mercury.	4. Platinum.	7. Ruthenium.
2. Silver.	5. Palladium.	8. Osmium.
3. Gold.	6. Rhodium.	9. Iridium.

If a strictly natural order were to be followed in grouping the elements, it would, however, be necessary to modify the foregoing arrangement. This will be rendered evident by pointing out the most important natural groups into which the elementary bodies admit of being subdivided. The detailed indication of the points of resemblance between the members composing each group must be deferred until the properties of the group are considered. In many instances these natural relations between the individual elements thus grouped together are very striking, in others they are more obscurely marked, and in the case of the metals of the earths proper, as well as of the noble metals, the natural chemical relations of these elements with the others are as yet but incompletely known. Aluminium, which should be classed with gallium as a triad, is often regarded as a tetrad from the vapour density of its chloride corresponding to the formula Al_2Cl_6, but as this compound has a very high boiling point, it is not improbable that, at a sufficiently high temperature, its vapour density would be found to be that required by the formula $AlCl_3$, especially as an organic methyl compound is known whose vapour density corresponds to the formula $Al(CH_3)_3$, in which aluminium is undoubtedly a triad. Manganese is the only heptad at present known. As osmium and ruthenium form tetroxides, OsO_4 and RuO_4, they might perhaps be regarded as octads: no octochloride is known, however. In the table which follows, the principal elementary bodies are represented in two converging series.

MONADS.

Fluorine.

Chlorine.
Bromine.
Iodine.

DYADS.

Oxygen.

Sulphur.
Selenium.
Tellurium.

TRIADS.

Boron. | Aluminium.
Gallium.
Rhodium. | Indium.
Gold. | Thallium.

TETRADS.

Carbon. | Cerium.
Ruthenium.
Silicon. | Iridium.
Zirconium. | Lead.
Titanium.
Tin. | Palladium.
Platinum.

PENTADS.

Nitrogen.

Phosphorus.
Vanadium.
Arsenicum. | Tantalum.
Antimony. | Niobium.
Bismuth.

HEPTADS.

Manganese.

MONADS.

Hydrogen.

Cæsium. | Silver.
Rubidium.
Potassium.
Sodium.
Lithium.

DYADS.

Barium.
Strontium. | Mercury.
Calcium. | Copper.

Magnesium.
Zinc.
Cadmium.

Glucinum.
Yttrium.
Erbium.
Terbium.
Lanthanum.
Didymium.
Thorinum.

TETRADS.

Iron. | Nickel.
Cobalt.

HEXADS.

Chromium.
Uranium.

Molybdenum.
Tungsten.
Osmium.

CHAPTER II.

A. FIRST DIVISION.—THE NON-METALS.

(339) **Non-Metals.**—The following table gives a general view of some of the most important of the constants of the non-metals. The squares employed in the column headed "Atomic Volume," indicate the relative volumes occupied by a quantity in grammes of each of the different elements in the gaseous condition, corresponding to the numbers given in the column of "Atomic Weight," assuming that the space occupied by one gramme of hydrogen under similar circumstances of temperature and pressure would fill a space of one square or one volume. One gramme of hydrogen at 0° and 760$^{mm.}$ pressure, occupies a space of 11·16345 litres.

TABLE OF NON-METALS.

NAME.	Symbol.	Atomic Weight.	Atomic Volume.	Relative wt. H=1.	Density. Gaseous. Theory.	Density. Gaseous. Expt.	Density. Solid.	Fusing point. °C.	Fusing point. °F.	Boiling point. °C.	Boiling point. °F.
Hydrogen ...	H	1	□	1	0·0692	0·0692					
Chlorine ...	Cl	35·5	□	35·5	2·4566	2·47				−33·6	
Oxygen ...	O	16	□	16	1·1072	1·1056					
Nitrogen ...	N	14	□	14	0·9688	0·9714					
Carbon .	C	12	?				3·336	never fused.			
Bromine ...	Br	80	□	80	5·536	5·54	3·18829*	−24·5	−12·1	59·5	139·1
Iodine ...	I	127	□	127	8·7884	8·716	4·947	107	225	175	347
Fluorine ...	F	19	□	19?	1·3148						
Sulphur ...	S	32	□	32	2·2144	2·23	2·0748	113	235·5	440	824
Selenium ...	Se	79·1	□	79·1	5·4737	5·68	4·788	217	423	below redness.	
Tellurium ...	Te	129	□	129	8·9268	9·00	6·1–6·33	about 500	932	?	
Phosphorus	P	31	□	62	4·2904	4·35	1·83676	44	111·5	278	532·4
Silicon ...	Si	28	?				2·49	?			
Boron ...	B	11·0	?				2·63	?			

* Sp. gr. of liquid at 0° C.

HYDROGEN: H = 1.

Density 0·06927;* *Atomic Volume* □; *Molecule in free state* HH □;† *Rel. wt.* 1; *Monad.*

(340) This element is not found in nature in a free state, but is one of the principal constituents of water. It also occurs in many other compounds, besides being present to a large extent in the organized beings which form the animal and vegetable kingdoms.

Preparation.—1. By passing an electric current from a voltaic battery through water acidulated with sulphuric acid so as to increase its conducting power, a gas is evolved from the platinode or negative plate, which is found on examination to be inflammable; at the other pole another gas is obtained which is not inflammable, but is a supporter of combustion, and is termed oxygen (345). To the former gas the name of *hydrogen* (from ὕδωρ, water, γεννάω, to generate) has been given. Oxygen and hydrogen are the sole constituents of water, and this liquid is reproduced by their union in the proportion of two volumes of hydrogen to one volume of oxygen.

2.—Hydrogen may also be obtained from water by the action of potassium or sodium. If a piece of the metal of the size of a pea be wrapped up in blotting paper, and rapidly introduced beneath the mouth of a strong wide tube, 10 or 12 inches (25 or 30 cm.) long, filled with water, and inverted in the pneumatic trough, bubbles of gas will be rapidly disengaged, and will collect in the upper part of the tube. On inverting the tube and applying a light, the gas will take fire and burn with flame; the liquid in the tube will be found to be alkaline, and will change the

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* Probably this number is a little too high in consequence of the presence of a small quantity of air in the hydrogen, the great diffusibility of the gas rendering it extremely difficult to prevent admixture of atmospheric air.

† *Molecular* formulæ will always be employed where it is practicable. Such molecular formulæ will indicate quantities of each compound, the volumes of which amount to double the combining volume of hydrogen, if the atom of hydrogen H = 1; as, for example:

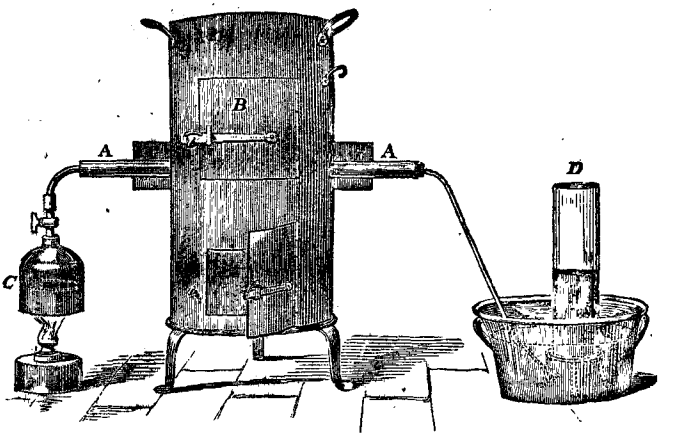
	Equal vols.		Molecular weight.		Molecular volume.
Free hydrogen . . .	HH	=	2	...	□
Free oxygen	OO	=	32	...	□
Free chlorine	ClCl	=	71	...	□
Free nitrogen	NN	=	28	...	□
Hydrochloric acid . . .	HCl	=	36·5	...	□
Steam	OH_2	=	18	...	□
Sulphuretted hydrogen . .	SH_2	=	34	...	□
Seleniuretted hydrogen . .	SeH_2	=	81·5	...	□

yellow colour of turmeric to brown, sodic hydrate having been formed by the displacement of half of the hydrogen in the molecule of water by the equivalent of sodium: $2OH_2 + Na_2 = 2NaHO + H_2$.

A convenient method of preparing hydrogen by this process, is to force the sodium into a small piece of glass tube about $\frac{3}{4}$ of an inch (20 mm.) long and $\frac{3}{16}$ of an inch (5 mm.) wide, and sealed at one end. The tube thus charged is thrown into a basin of water, and an inverted jar filled with water placed over it; in this way the water comes slowly in contact with the metal, and a regular stream of bubbles of hydrogen rises into the inverted vessel.

3.—Hydrogen may also be obtained by the action of water on iron at a high temperature. For this purpose a piece of iron

FIG. 275.



tubing, shown at A A, fig. 275, is filled with iron turnings or nails, and heated to redness in a furnace, B, whilst a current of steam from a small boiler, C, is passed through the tube; a portion of the aqueous vapour in its passage is decomposed, the oxygen entering into combination with the heated iron, forming magnetic oxide of iron, whilst the liberated hydrogen passes on with the excess of steam, and may be collected over water in a jar, D, placed over the mouth of a bent tube attached to the other extremity of the iron pipe. The decomposition may be represented in symbols as follows:

$$3Fe + 4OH_2 = FeO.Fe_2O_3 + 4H_2.$$
$$[Fe_3 + 4OH_2 = {}^{iv}(Fe_3)^{viii}O_4 + 4H_2.]$$

4.—Deville and Debray prepare nearly pure hydrogen on a

large scale, by passing steam over charcoal, or coke, heated to dull redness. Carbonic anhydride and hydrogen are the sole products if the temperature be kept sufficiently low:

$$2OH_2 + C = 2H_2 + CO_2.$$
$$[2OH_2 + C = 2H_2 + CO_2.]$$

The gas is purified by causing it to traverse an apparatus filled with slaked lime, similar to that known as the dry lime purifier for coal-gas. If the temperature be allowed to rise too high, part of the carbonic anhydride is converted into carbonic oxide (386), which cannot be removed from the mixture by lime, so that the hydrogen, under these circumstances, is rendered more or less impure.

5.—Hydrogen may also be obtained by heating zinc with a solution of potassic or sodic hydrate, the metal displacing the hydrogen contained in the hydrate, whilst the zinc compound formed remains dissolved in the alkaline liquid,

$$2KHO + Zn \text{ becoming } K_2ZnO_2 + H_2.$$

This method is interesting from its theoretical bearings rather than from any practical utility.

6.—According to Lorin (*Compt. Rend.*, 1865, lx. 745), an aqueous solution of ammonia at 40° (104° F.) attacks zinc and even iron with evolution of hydrogen, whilst with zinc or iron, free ammonia, and an ammonic salt, such as the sulphate or chloride, the gas is generated as rapidly as with zinc and dilute sulphuric acid, so that advantage may be taken of this reaction for obtaining hydrogen.

7.—The most convenient way of preparing hydrogen, however, is by the action of dilute sulphuric acid on zinc. The zinc may be *granulated*, or reduced into grains or flakes, by melting it in an iron ladle, and pouring it into a large pan of cold water.* About half an ounce (15 grms.) of the granulated zinc is introduced into a retort, and about 7 ounces (200 c. c.) of dilute sulphuric acid, prepared by cautiously pouring one part of the concentrated acid into 6 parts of cold water, with constant stirring, is poured upon the zinc. Hydrogen gas is soon evolved in great

* If the melted metal be poured from the height of a yard or more above the surface of the water, the granules are spongy and very thin, presenting a large surface compared with their weight; whilst solid heavy granules are obtained if the zinc be poured at the distance of a few inches only above the water. The former kind is most convenient when a rapid current of hydrogen is required.

abundance: the first portions of gas, being contaminated with the air contained in the retort, must be allowed to escape; afterwards the gas may be collected in the usual way. In this process the zinc may be regarded as displacing the hydrogen of the acid, forming the salt called sulphate of zinc, or zincic sulphate, which becomes dissolved, whilst the hydrogen passes off in the gaseous form. The change may be illustrated by the following equation:

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Zincic sulphate.}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}.$$

$$[SO_2(OH)_2 + Zn = SO_2(O_2Zn)'' + H_2.]$$

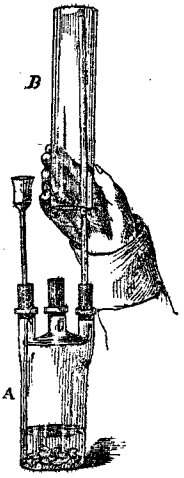
An ounce of zinc is sufficient to liberate from the acid about 2½ gallons of the gas, or 30 grms., will furnish about 10 litres. Scraps of iron may be substituted for zinc; but in this case the gas is less pure: it has a disagreeable odour, due to the presence of compounds of hydrogen and carbon, but these may be removed by passing the gas through a tube filled with fragments of wood-charcoal (Stenhouse). The gas furnished by the action of dilute sulphuric acid on zinc also possesses a peculiar odour, and is frequently contaminated with small quantities of compounds of hydrogen with sulphur and arsenicum. It may be freed from these impurities by causing it to pass first through a strong solution of potassic hydrate, then through a solution of mercuric chloride or argentic nitrate, and finally, through concentrated sulphuric acid to remove moisture. A solution of potassium permanganate may be substituted for the metallic solution with advantage.

Properties.—Hydrogen is an elementary substance, discovered in 1766 by Cavendish, who called it *inflammable air*. When prepared with the precautions just mentioned, it is a colourless, transparent, tasteless, and inodorous gas. Its refractive power upon light is higher than that of any other gas, being more than six times as great as that of atmospheric air at the same temperature, when the hydrogen is compressed until its weight is the same as that of an equal bulk of air. It has never been liquefied, and is very slightly soluble in water, 100 volumes of water, according to Bunsen, dissolving 1·93 vols. of hydrogen at all temperatures between 0° and 24° (32° and 75°·2 F.) Hydrogen is the lightest form of matter which is known: its weight is only one-sixteenth of that of an equal bulk of oxygen, and a little less than a fourteenth of that of air; 1 litre at 0° C. and 760^{mm}· Bar. weighs 0·089578 gram., or 100 cubic inches of it at 60° F. and 30 in. Bar., weigh but 2·143 grains. Owing to its levity, it has been extensively used for aërostatic purposes, although the facility with which

coal-gas can now be obtained has caused this latter, notwithstanding its much greater density, to be universally substituted for hydrogen in filling balloons.

A light bag made of the craw of a turkey, or of collodion, may easily be inflated with hydrogen, and will ascend rapidly, carrying with it a weight of several grains. Owing to the lightness of the gas, a jar may be easily filled with it by *displacement* without using the pneumatic trough:—A tube, 8 or 10 inches (20 or 25 centimetres) long, is fixed by a cork, in the manner shown at A, fig. 276, into a three-necked bottle containing some granulated zinc; dilute sulphuric acid is introduced through the funnel, and the gas, after the atmospheric air in the bottle has been allowed to escape, may be collected by holding a jar over the tube, as at B. The hydrogen will be retained for some minutes even, if the jar be removed, provided that it be still kept in an inverted position, although if the mouth be turned upwards, the gas will escape in the course of a few seconds.

FIG. 276.



Hydrogen is extremely inflammable; when a lighted taper is plunged into a jar of it, the gas takes fire but the taper is extinguished. A jet of hydrogen burns in air with a pale yellowish, feebly luminous flame of a very high temperature.

Pure hydrogen, although it cannot support life, is not poisonous, and when mixed with a certain proportion of oxygen may be breathed for some time without inconvenience; but owing to its rarity, it renders the voice temporarily much sharper and more shrill than usual.

Hydrogen unites directly with several elements if heated with them, particularly with oxygen and with chlorine. If heated with sulphur, bromine, or phosphorus, it also combines, although slowly and with difficulty.

Many metals, as iron, nickel, manganese, potassium, sodium, and especially platinum and palladium, absorb many times their volume of hydrogen gas, which is then said to be occluded; in some instances the hydrogen merely is dissolved by the metal in the same way that it dissolves in a liquid, whilst in others, as with potassium and sodium, it seems to form definite compounds.

Hydrogen has a smaller combining number than any other elementary body, and on this account has been taken as the unit or standard of comparison, both for atomic weights and combining volume. Its proportional number is therefore unity, or 1, and its combining volume 1 or □.

The proportion in which the different elements combine with hydrogen to form gaseous compounds affords a well-marked character which serves as a foun-

dation for grouping the different elements into natural families. For example, in the table which follows, some of the most important gaseous compounds of the different elements with hydrogen are enumerated: in each case, the quantity represented by the formula given indicates 2 volumes of the gaseous compound (H = 1 vol. □, and HH = 2 vols. □).

Compounds with Monads.	Compounds with Dyads.	Compounds with Triads.	Compounds with Tetrads.
Hydrochloric Acid. HCl	Water. H_2O	Ammonia. H_3N	Marsh Gas. H_4C
Hydrobromic Acid. HBr	Sulphuretted Hydrogen. H_2S	Phosphuretted Hydrogen. H_3P	Sliciuretted Hydrogen. H_4Si
Hydriodic Acid. HI	Seleniuretted Hydrogen. H_2Se	Arseniuretted Hydrogen. H_3As	
Hydrofluoric Acid. HF	Telluretted Hydrogen. H_2Te	Antimoniuretted Hydrogen. H_3Sb	

In the first column the compounds are formed by the union of one atom of each element. The metallic basyls of the alkalies and one or two other metals displace hydrogen from its compound with chlorine, in the proportion of single atoms, and these metals, with the halogens themselves, constitute the group of *Monads*.

In the second column of the table two atoms of hydrogen are shown in combination with one atom of certain other (*dyad*) elements. In addition to the non-metallic elements which thus have the power of supplying the place of two atoms of chlorine in combining with hydrogen, it may be stated that the metals of the alkaline earths and the ordinary metals which form basic oxides, displace two atoms of hydrogen, and unite with two atoms of chlorine; they constitute the *dyad* group of metals.

In the third column of the table each compound given contains 3 atoms of hydrogen united with 1 atom of some other (*triad*) element. These also have their representatives among the metals; for the triads embrace gold and rhodium, an atom of each of which unites with three atoms of chlorine, and is thus equivalent in function to three atoms of hydrogen.

In the fourth column the compounds enumerated contain four atoms of hydrogen in combination with another (*tetrad*) element. Among the metals, platinum, tin, and a few other rarer elements discharge the functions of four atoms of hydrogen, each atom of the metal forming a stable compound with 4 atoms of chlorine.

CHAPTER III.

CHLORINE: Cl = 35·5.

Theoretic density 2·4566; *Observed density taken at* 200° (392° F.) 2·4502*; *Atomic vol.* □; *Molecule in free state* ClCl □; *Rel. wt.* 35·5; *Monad as in* HCl.

(341) Chlorine, the most important member of the group of halogens,† was discovered by Scheele in 1774. It is abundantly met with in combination with sodium, constituting ordinary table salt. This necessary of life occurs plentifully in beds in various parts of the world, and is the most abundant of the saline bodies existing in the waters of the ocean. It contains 60·68 per cent. of chlorine.

Preparation, 1.—Chlorine is employed on an enormous scale in the manufacture of bleaching powder, or chloride of lime. It is generally prepared in capacious stills, sufficiently large to hold 200 gallons or about 900 litres of liquid; these are usually made of Yorkshire flags clamped together with ironwork, and the joints rendered tight by vulcanized caoutchouc. The lower part of these stills is enclosed in a case through which a current of steam is passed. Hydrochloric acid solution, of specific gravity from 1·160 to 1·170 (which is obtained as a waste product in the manufacture of sodic carbonate from sea-salt), is run through a curved funnel into the stills, previously charged with oxide of manganese in small lumps. The hydrogen of the acid unites with the oxygen of the oxide of manganese to form water, whilst one-half of the chlorine combines with the manganese and the other half escapes in the gaseous form. The ultimate result of the reaction may be illustrated by the following symbols:

$$\underset{\text{Manganic dioxide.}}{MnO_2} + \underset{\text{Hydrochlor. acid.}}{4HCl} = \underset{\text{Manganous chloride.}}{MnCl_2} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Chlorine.}}{Cl_2}.$$

This transformation takes place in two stages, the first consisting

* This agrees very closely with the theoretic density 2·45012 corresponding to the equivalent 35·457 for chlorine, the result of the laborious researches of Stas.

† The group of *halogens* consist of the elements fluorine, chlorine, bromine, and iodine, which are closely allied to one another. They form with metals compounds analogous to sea salt, and from this circumstance the name halogens or salt-producers (from ἅλς, sea-salt) has been applied to them.

in the conversion of the manganic oxide into manganic chloride, $MnCl_4$:

$$MnO_2 + 4HCl = 2OH_2 + MnCl_4.$$

which by elevation of temperature, decomposes into manganous chloride and free chlorine,

$$MnCl_4 = MnCl_2 + Cl_2.$$

This process is usually resorted to for the preparation of the gas on the small scale in the laboratory. Three ounces or 100 grams of black oxide of manganese in small lumps with half a pint (350 cub. centim.) of the commercial muriatic acid will yield between 3 and 4 gallons (about 15 litres) of the gas on gently heating the mixture. Care should be taken not to use an acid more dilute than 1·15 in the preparation of the gas; since, owing to a neglect of this precaution, explosions have in some instances occurred in operating on the large scale. Hypochlorous acid, or one of the explosive oxides of chlorine, was probably formed in these cases.

An important improvement in the manufacture of chlorine on a large scale has taken place in the introduction of Weldon's process for regenerating the manganese oxide from the manganese chloride left in the chlorine stills. The slightly acid liquid is neutralized by the addition of excess of calcic carbonate, which precipitates the iron and aluminia, and after being allowed to settle, the clear liquid containing chlorides of manganese and calcium is run off into an apparatus called the "oxidizer," where it is mixed with an excess of calcic hydrate, in the proportion of about 1·2 to 1·4 mol. of calcium to 1 of manganese, and oxidized by blowing air through the mixture, whilst the temperature is maintained at about 55°—75° (131°—167° F.). During the operation, a further quantity of milk of lime is run in, so that the total may be in the proportion of 1·5 to 1·6 mols. of calcium to each mol. of manganese. In this way the manganese is peroxidized and precipitated as a thin black mud, having approximately the composition $CaMnO_3.H_2MnO_3$; this is allowed to settle as far as possible, and then drawn off and used for the manufacture of chlorine in the ordinary way. This regenerated oxide is not only much more readily attacked than the native, but requires a smaller expenditure of hydrochloric acid to produce the same amount of chlorine.

2.—Chlorine may also be easily obtained from a mixture of 10½ parts by weight of sulphuric acid, previously diluted with 7 parts of water and allowed to cool, and 4 parts of pounded sodic chloride mixed intimately with 3 parts of finely pulverized black oxide of manganese. In this case the whole of the chlorine is expelled in the gaseous state, the sodium remaining in the form of hydric sodic sulphate, and the manganese in that of manganous sulphate, whilst the oxygen of the oxide is separated in the form of water produced by combination with hydrogen derived

from the sulphuric acid. The decomposition may be represented as follows:

$$\underset{\text{Manganic dioxide.}}{MnO_2} + \underset{\text{Sodic chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} = \underset{\text{Manganous sulphate.}}{MnSO_4} + \underset{\text{Hydric sodic sulphate.}}{2NaHSO_4} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Chlorine.}}{Cl_2}.$$

$$MnO_2 + 2NaCl + 3SO_2(OH)_2 = SO_2(O_2Mn)'' + SO_2(OH)(ONa) + 2OH_2 + Cl_2.$$

The gas comes off slowly in the cold, but freely on the application of a gentle heat. A little hydrochloric acid is always formed in this reaction: but it may be removed in great part from the chlorine by allowing the gas to bubble up through a vessel containing water, in the manner shown in fig. 307, where a similar apparatus is employed for carbonic oxide. It is, however, always very difficult to remove the last traces of hydrochloric acid from chlorine prepared either by this or the previous methods, by simply washing the gas with water. When required quite free from hydrochloric acid, it should be washed first with a tolerably concentrated solution of cupric sulphate, and then with water (Stolba, *Chem. Centr.*, 1874, 116).

3.—Another process has been introduced by Deacon for the manufacture of chlorine on a large scale, but the observance of many minute details is necessary to insure success. The method consists in passing a mixture of hydrochloric acid and air (as it comes from the salt cake furnaces) through a brickwork chamber containing fragments of firebrick which have been saturated with a solution of cupric sulphate or cupric chloride. The copper salt appears to undergo no chemical change, but determines by its presence the decomposition of the hydrochloric acid by the oxygen of the air, water being produced and chlorine liberated. The temperature at which the transformation takes place is between 371° and 461° (700° and 750° F.) (*Journ. Chem. Soc.*, 1872, xxv. 725). According to Hasenclever (*Deut. chem. Ges. Ber.*, 1876, ix. 1070), however, although the results obtained are satisfactory at first, 60 per cent. of the hydrochloric acid being converted into chlorine, the action after a time diminishes rapidly in intensity, until scarcely any of the hydrochloric acid is decomposed. The cause of this appears to be the gradual accumulation of sulphuric acid, carried over mechanically from the salt cake furnaces.

Properties.—Chlorine is a transparent gas of a greenish yellow colour (whence the name is derived, from χλωρὸς, green), and of a powerful suffocating odour. It produces, when breathed, even if largely diluted with air, distressing irritation of the air

passages, attended with coughing. It is much heavier than air; a litre at 0° C. and 760$^{mm.}$ weighs 3·1808 grams, or 100 cubic inches at 60° F. and 30 inches Bar. weigh 76·3 grains. At a temperature of −40° (−40° F.) under the ordinary atmospheric pressure, or at 0° (32 F.) under a pressure of 6 atmospheres, it is condensed to a yellow limpid liquid, of density about 1·33, which boils at −33°·6 (−28°·3 F.); it does not conduct electricity, and remains unfrozen even at the cold of −140° (−220° F.). Chlorine is soluble in about half its bulk of cold water, and the solution, which is readily formed by agitating the gas and water together, has the colour, odour, and astringent taste of the gas. According to Schönfeld (*Ann. Chem. Pharm.*, 1855, xcv. 8), water at 10° (50° F.) dissolves 2·585 times its bulk of the gas; at 15° (59° F.) 2·368, and at 40° (104° F.) 1·365 times its bulk. Chlorine, in consequence of this solubility, cannot be advantageously collected over cold water, and mercury is acted upon by the gas with great rapidity. It is necessary, therefore, either to use warm water in the pneumatic trough, or to collect the gas by the process of displacement in dry bottles. With water, chlorine forms a definite *hydrate* $Cl_2,10OH_2$, which may be readily obtained in the crystalline state by passing a current of chlorine through a mixture of crushed ice and water. It has been thought that this compound might really be represented by the formula $(ClHO + HCl + 9OH_2)$; this, however, is unlikely, as hypochlorous acid discolours the epidermis, whilst the hydrate does not. Moreover, neither hydrochloric acid nor hypochlorous acid alone forms a crystalline hydrate, at that temperature. This hydrate, if it be enclosed in hermetically sealed tubes, furnishes a ready method of obtaining liquefied chlorine, since it decomposes at 38° (100°·4 F.) into water and free chlorine, which under its own pressure condenses to a liquid, forming a layer at the bottom of the saturated aqueous solution of chlorine in the tube.

Chlorine is not combustible, and it does not combine directly with oxygen. A taper burns in it with a reddish, smoky flame, the hydrogen of the combustible vapour of the wax or fat combining with the chlorine, whilst part of the carbon, for which its chemical attraction is but small, is deposited. Many bodies, however, take fire spontaneously when introduced into chlorine; this is the case with phosphorus; many of the metals do the same when in a finely divided state; amongst them are copper leaf, finely powdered antimony, and arsenicum. A great number of organic substances rich in hydrogen are decomposed by chlorine, sometimes with such energy as to inflame them; a bit of paper

or cotton-rag dipped into oil of turpentine and plunged into the gas bursts into flame, and deposits an abundance of soot.

The action of chlorine upon bodies containing hydrogen is often of a very peculiar kind. It combines with part of the hydrogen, and withdraws it from the combination; each atom of hydrogen uniting with an atom of chlorine to form hydrochloric acid, HCl, whilst, at the same time, for each atom of hydrogen so withdrawn from the original compound, an atom of chlorine is substituted. Most of the vegetable colouring matters contain hydrogen, and are decomposed by chlorine; whilst colourless, or nearly colourless, compounds containing chlorine are formed in the place of the coloured compounds with hydrogen. If a solution of chlorine be mixed with some of the blue liquid formed by dissolving indigo in sulphuric acid, or with ordinary writing ink, or with tincture of litmus, the colour will in each case be immediately and almost completely discharged, and it cannot be subsequently restored.

Another valuable property of chlorine is its disinfecting power,—that is, its power of destroying noxious vapours and miasmata; it is sometimes employed for this purpose in fumigating buildings after the occurrence of contagious diseases.

Uses.—Besides the application of chlorine on the large scale, in bleaching and for disinfecting purposes, it is in continual requisition in the laboratory as an oxidizing agent and for preparing chlorine derivatives of carbon compounds: owing to its attraction for hydrogen it readily decomposes water, and liberates oxygen, which at the moment that it is set free enters readily into combination; it is principally to this action that its bleaching properties are due. The preparation of potassic chlorate (361), of ferric acid, and of the sesquioxides of cobalt and nickel, afford illustrations of this mode of employing it; and, in researches upon the nature of many products furnished by organic chemistry, it often, as in the series of compounds obtained from ethylenic di-chloride, is used as a means of throwing light upon their molecular constitution.

Chlorides.—Chlorine combines with all the non-metals, uniting spontaneously with many of them, and forming compounds of great importance; it also enters into combination with all the metals, several of which it attacks energetically at ordinary temperatures, exhibiting the usual phenomena of combustion; the compounds which it forms are termed *chlorides*. With the exception of argentic chloride, and mercurous and cuprous chlorides, they are all more or less soluble in water. The lower chlorides of gold and platinum, and chloride of lead are but

sparingly soluble, especially the former two. It frequently happens that chlorine combines with the same metal in more than one proportion: for example, with iron, ferrous chloride, $FeCl_2$, and ferric chloride, Fe_2Cl_6, may be formed; with platinum, platinous chloride, $PtCl_2$, and platinic chloride, $PtCl_4$ (formerly distinguished as the bichloride) may be obtained; and generally, for each basic oxide of the metal, a corresponding chloride exists.

Chlorine, when in solution in the uncombined form, is easily recognised by its odour and its bleaching properties. Whether free, or combined with a metal, the addition of a solution of argentic nitrate produces a white curdy flocculent precipitate of argentic chloride which changes to violet on exposure to the light. The white precipitate is easily dissolved on adding a small quantity of solution of ammonia, but it is insoluble in nitric acid. When free chlorine acts upon argentic nitrate in the presence of water, a small quantity of chlorate is formed at the same time as the chloride, nitric acid being liberated: $3Cl_2 + 6AgNO_3 + 3OH_2 = 5AgCl + AgClO_3 + 6HNO_3$.

(342) **HYDROCHLORIC ACID**: *Muriatic Acid, Hydric chloride,* $HCl = 36{\cdot}5$; *Theoretic Density,* 1·2629: *Observed,* 1·2474; *Atomic and Mol. Vol.* [ ]; *Rel. wt.* 18·25.—The most important of the compounds of chlorine with the non-metals is that which it forms with hydrogen. The two gases may be mixed in equal volumes, and they will remain without action upon each other, if kept in the dark, but the moment that they are brought into direct sunlight they unite with a powerful explosion, and a colourless, intensely acid gas is the product. This sudden combination is also effected by the action of the electric light and of that produced by the combustion of a mixture of nitric oxide and carbonic bisulphide vapour. In diffused daylight the combination takes place gradually; but the application of a lighted match, or the passage of the electric spark through the mixture, instantly determines its explosion. One volume of chlorine thus unites with 1 volume of hydrogen, producing 2 volumes of hydrochloric acid, no condensation occurring in the act of union. The composition of hydrochloric acid is consequently the following:

			By weight.		By vol.
Chlorine	... Cl	= 35·5	or 97·26	...	1
Hydrogen	... H	= 1·0	2·74	...	1
Hydrochloric acid	HCl	= 36·5	100·00	...	2

So powerful is the attraction of chlorine for hydrogen, that if either a solution of chlorine in water, or the gas itself in a moist state, be exposed to the sun's rays, hydrochloric acid is

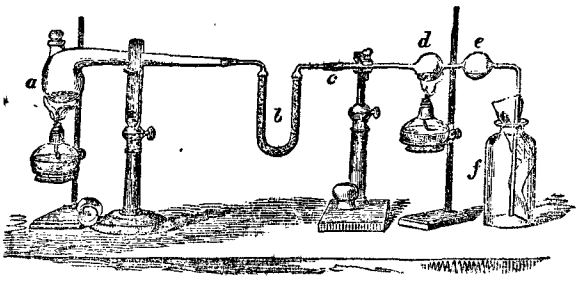
formed, and the oxygen of the water is liberated: in the dark, however, chlorine has no power to decompose water.

If moist chlorine be passed through a red-hot porcelain tube, hydrochloric acid is formed, and oxygen is set free; $2OH_2 + 2Cl_2 = 4HCl + O_2$; although, on the other hand, when hydrochloric acid gas is mixed with air and passed through an ignited porcelain tube, chlorine is liberated and water produced.

The composition of hydrochloric acid may be analytically determined by heating sodium in a measured volume of the gas. The metal burns vividly, and liberates a quantity of hydrogen, the volume of which is one-half of that of the hydrochloric acid; common salt being formed at the same time. Analogous results are obtained if iron or tin be substituted for sodium; ferrous or stannous chloride is formed, whilst hydrogen is set at liberty. As Hofmann has shown, the decomposition may also be effected, at the ordinary temperature, by agitating a given measure of dry hydrochloric acid gas with an amalgam of sodium, introduced into the gas as it stands over mercury. In a few minutes the volume is reduced to one-half, and pure hydrogen is left.

The presence both of hydrogen and of chlorine in the acid gas is easily shown by the following experiment (Graham). The hydrochloric acid generated in the retort, *a*, fig. 277, by the

Fig. 277.



action of sulphuric acid on sodic chloride, is dried by being passed through a tube, *b*, filled with calcic chloride: this tube is connected by a vulcanized caoutchouc joint, *c*, with a tube upon which two bulbs have been blown: in the first of these, *d*, some pounded anhydrous black oxide of manganese is placed: a piece of litmus-paper inserted in the bottle, *f*, which receives the escaping gas, is quickly reddened. On applying heat to the bulb, *d*, containing the oxide, manganous chloride is produced, and as it is not volatile, it remains in the bulb, whilst water is formed and becomes condensed in the second bulb, *e*; in the meantime free chlorine passes on into the bottle, *f*, showing itself by its peculiar

colour and its bleaching effect upon the litmus-paper. The reaction is represented by the following symbols: $4HCl + MnO_2 = 2OH_2 + MnCl_2 + Cl_2$.

Preparation.—Hydrochloric acid gas is easily prepared by introducing fragments of common salt (which has been fused in a crucible at a red-heat and then poured out on to an iron plate and allowed to cool) into a glass retort, and adding to it twice its weight of oil of vitriol. A far more convenient method, however, is to employ slightly diluted sulphuric acid as suggested by Gregory. Twelve parts of common salt are added to a cold mixture of 20 parts by weight of oil of vitriol and 8 of water, or 11 parts by measure of sulphuric acid and 8 of water, contained in a retort, or flask, furnished with a bent glass tube: this mixture evolves scarcely any hydrochloric acid at the ordinary temperature, but when gently heated, the gas escapes in abundance, and may be collected either over mercury, or by displacement of the air from dry bottles. An ounce, or 30 grms., of salt yields about 700 cubic inches (12 litres) of the gas. In this case half the hydrogen of the sulphuric acid is displaced by the sodium of the sodic chloride forming hydric sodic sulphate, whilst the displaced hydrogen and the chlorine of the sodic chloride unite to form hydrochloric acid, as is shown in the following equation:

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$
$$[NaCl + SO_2(OH)_2 = HCl + SO_2(OH)(ONa)].$$

Hydrochloric acid may also be obtained in a gaseous state by placing the ordinary concentrated aqueous solution in a retort or flask furnished with a delivery tube, and allowing concentrated sulphuric acid to drop in slowly by means of a funnel provided with a tap.

Properties.—Hydrochloric acid is a colourless gas, of a peculiar, pungent odour, and an intensely acid taste; it irritates the eyes, and produces coughing if breathed, even when largely diluted. It is also very injurious to vegetation, causing the leaves to shrivel and turn brown. It is heavier than air; 1 litre of the gas at 0° C. and $760^{mm.}$ weighs 1·6352 grams, or 100 cubic inches at 60° and 30 inches Bar. weigh 39·23 grains. Under a pressure of 40 atmospheres at 10° (50° F.) it becomes condensed to a colourless liquid of density 1·27, which dissolves bitumen; it has never been frozen; the refracting power of this liquid is less than that of water. Hydrochloric acid gas is incombustible, and it extinguishes burning bodies. It reddens dry litmus-paper. When allowed to escape into the air it produces white fumes by condensing the atmospheric moisture, and forming with it a body less volatile

than pure water. It is instantly absorbed by water, so that if a vessel filled with the gas be opened under water, the latter rushes in as into a vacuum; and similarly a lump of ice introduced into a jar of the gas standing over mercury liquefies and absorbs the hydric chloride with great rapidity.

(343) **Solution of Hydrochloric Acid.**—The solution of hydrochloric acid in water is an indispensable reagent in the laboratory. It is easily prepared for use by passing the gas obtained in the manner before mentioned into water. The retort or flask is connected with a couple of Woulfe's bottles; in the first a small quantity of water is placed to detain any impurities which might be carried over mechanically with the gas; the second bottle may contain 4 parts of water for 3 of sodic chloride employed, and should be immersed in a vessel of cold water, as the condensation of the gas is attended with great development of heat. On applying a gentle heat to the retort, the gas comes over and is absorbed by the water, whilst the easily soluble hydric sodic sulphate remains in the retort, as explained above. Hydrochloric acid solution, however, is but seldom prepared in the laboratory, the decomposition being effected on the manufacturing scale in iron cylinders, like those employed in the preparation of nitric acid (399), but only one-half the quantity of sulphuric acid prescribed above is used, and a higher temperature is applied than when glass vessels are employed; $2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$: [$2NaCl + SO_2(OH)_2 = 2HCl + SO_2(ONa)_2$]. The sulphuric acid in this case is in the proportion of one equivalent to each equivalent of salt; the normal sodic sulphate produced remaining in the cylinder, whilst the hydrochloric acid is absorbed by water contained in a series of salt-glazed stone-ware jars, arranged as Woulfe's bottles. Hydrochloric acid is produced in enormous quantities in the manufacture of salt cake, and is absorbed in large towers filled with bricks or coke over which a stream of water trickles; the impure solution thus obtained is extensively employed in the arts, particularly in the preparation of chlorine as a preliminary to the manufacture of chloride of lime and potassic chlorate. It is also largely used as a solvent for tin by the dyer and calico printer, as well as in the manufacture of sal ammoniac.

Water at 4° (39°·2 F.) absorbs ·804 of its own weight, or about 492 times its bulk of hydrochloric acid gas, increasing in volume about one-third, and acquiring a density of 1·2265.* The

* Water at 0° (32° F.), according to Roscoe and Dittmar, dissolves 0·825 of its weight of hydrochloric acid gas, under a pressure of $760^{mm.}$ of mercury; and

solution is a colourless, fuming liquid, which by a slight elevation of temperature, parts with the gas abundantly; at this strength it contains more than 44 per cent. of acid, which is about the proportion indicated by the formula, $HCl.3OH_2$.

When a current of dry hydrochloric acid is passed into a concentrated aqueous solution of the acid cooled to a temperature below $-20°$ ($-4°$ F.) it is absorbed and crystals soon make their appearance, whilst the temperature rises to $-18°$ ($-0°{\cdot}4$ F.) at which it remains stationary as long as crystals continue to be deposited. These crystals are a definite hydrate of hydrochloric acid having the composition $HCl.2OH_2$: they decompose rapidly in the air, emitting white fumes (Pierre and Puchot, *Compt. Rend.*, 1876, lxxxii. 45).

If the strong acid be placed in a retort, and distilled, it loses hydrochloric acid, until the liquid which remains has a density of 1·100; at this point it distils unchanged. A weaker acid, when distilled, parts with its water freely until it acquires the density of 1·100 and then passes over unchanged, boiling at a temperature of 112° (233° F.). Such an acid contains about 20 per cent. of hydrochloric acid, and corresponds approximately in composition with the formula, $HCl.8OH_2$.* Common hydrochloric acid may therefore easily be purified by dilution until it has a density of 1·1 at 15°·5 (60° F.), and then distilling.† Bineau, by concentrating the acid *in vacuo* over sulphuric acid, at the ordinary temperature, obtained a hydrate, $HCl.6OH_2$, of density 1·128, containing 25 per cent. of the anhydrous acid. According to this observer (*Ann. Chim. Phys.*, 1843, [3], vii. 259), the vapour of the acid, density 1·10, has a sp. gr. of 0·69, 1 volume of the acid and 8 volumes of aqueous vapour being united without condensation; probably they exist merely in a state of admixture.

at 15°·5 (60° F.) it dissolves 0·745 of its weight (*Jour. Chem. Soc.*, 1859, xii. 128).

* Roscoe and Dittmar, (*loc cit.*) by varying the pressure under which the distillation is effected, have, however, shown that this apparent constancy of composition is really an accidental circumstance, and that there is no definite hydrate of this acid; but that for every pressure an aqueous solution exists, which, when distilled under that pressure, possesses a fixed composition and fixed boiling point. For example, when distilled under a pressure of $50^{mm.}$ of mercury, the distillate contained 23·2 per cent. of hydrochloric acid; distilled under $380^{mm.}$ pressure, the percentage of acid was 21·3, corresponding to the formula $2HCl.15OH_2$; whilst under a pressure of $760^{mm.}$ the per-centage of acid was reduced to 28·24, $HCl.8OH_2$: if distilled under a pressure of $1520^{mm.}$ or 2 atmospheres, the amount of acid fell to 19·0; and under $2280^{mm.}$ or 3 atmospheres, as low as 18·2 of HCl per cent.: the composition of the liquid in the last case corresponding nearly to $HCl.9OH_2$.

† Chlorine, however, if present, as well as arsenious chloride and sulphurous acid, passes over with the distillate.

Commercial hydrochloric acid has a yellow colour, and is liable to be contaminated with iron, and with the chlorides of sodium and arsenic, the latter derived from the sulphuric acid employed in its preparation. Sulphuric and sulphurous acids and free chlorine are also often present in it. According to Drec (*Chem. Centr.*, 1872, 418) the best method of removing arsenic from hydrochloric solution is to dilute it until it has a density of 1·13, digest it at 30° (86° F.) with metallic copper for some time and then to distil. The addition of about 5 per cent. of potassic hypophosphite to precipitate the arsenic, and subsequent distillation of the clear liquid is equally effective (Engel, *Compt. Rend.*, 1873, lxxvi. 1139). If pure, the acid should leave no residue when evaporated, and on saturating it with ammonia it should give no precipitate of ferric oxide; sulphuretted hydrogen should likewise produce no turbidity in it, which would be the case if arsenic, free chlorine, or sulphurous acid were present, and after dilution with three or four times its bulk of water, no white cloud of baric sulphate should be produced by the addition of baric chloride. Traces of sulphurous acid are also easily detected by Löwenthal's test, which consists in the addition of a mixture of ferric chloride and potassic ferricyanide: if sulphurous acid be present, Prussian blue is formed by the reducing action of the acid on the mixture.

Strength of Hydrochloric Acid (J. Kolb, *Compt. Rend.*, 1872, lxxiv. 737).

Density.	Hydrochloric acid in 100 parts at 0° C.	Hydrochloric acid in 100 parts at 15° C.	Density.	Hydrochloric acid in 100 parts at 0° C.	Hydrochloric acid in 100 parts at 15° C.
1·000	0·0	0·1	1·134	25·2	26·6
1·007	1·4	1·5	1·143	27·0	28·8
1·014	2·7	2·9	1·152	28·7	30·2
1·022	4·2	4·5	1·157	29·7	31·2
1·029	5·5	5·8	1·161	30·4	32·0
1·036	6·9	7·3	1·166	31·4	33·0
1·044	8·4	8·9	1·171	32·3	33·9
1·052	9·9	10·4	1·175	33·0	34·7
1·060	11·4	12·0	1·180	34·1	35·7
1·067	12·7	13·4	1·185	35·1	36·8
1·075	14·2	15·0	1·190	36·1	37·9
1·083	15·7	16·5	1·195	37·1	39·0
1·091	17·2	18·1	1·199	38·0	39·8
1·100	18·9	19·9	1·205	39·1	41·2
1·108	20·4	21·5	1·210	40·2	42·4
1·116	21·9	23·1	1·212	41·7	42·9
1·125	23·6	24·8			

The preceding table contains the amount by weight of hydrochloric acid in 100 parts of solutions of the acid of the various densities therein enumerated.

A solution of hydrochloric acid is decomposed by all the metals which decompose water at a red heat, the metal being dissolved, and hydrogen gas set free, just as when iron or zinc is acted upon by dilute sulphuric acid: for example, $2HCl + Zn = ZnCl_2 + H_2$.

(344) **Action of Hydrochloric Acid on Metallic Oxides.**—The action of hydrochloric acid upon the oxides of the metals is important. Almost all protoxides are dissolved by the acid, and appear to combine with it; but on evaporating the liquid, in most cases a saline compound is obtained in which neither hydrochloric acid nor the metallic oxide is present, and which contains neither hydrogen nor oxygen. When the hydrated oxide of a monad metal, such as sodic hydrate, is acted upon by hydrochloric acid, the hydrogen of the acid changes place with the metal, and is exactly sufficient with the hydroxyl, OH, of the hydrate to form water which remains in the solution or else evaporates on the application of heat, whilst the metal and the chlorine unite directly with each other forming a chloride, as is shown by the following symbols; $NaHO + HCl$ yield $NaCl + OH_2$.

When the anhydrous oxide of either a monad or a dyad is employed, the reaction is similar, but two atoms of hydrochloric acid are concerned, and the metal exchanges places with two atoms of hydrogen:

$$Tl_2O + 2HCl \text{ yield } 2TlCl + OH_2;$$
$$BaO + 2HCl \text{ yield } BaCl_2 + OH_2.$$

But although the metal may exist in solution in the form of chloride, this circumstance does not prevent its precipitation as oxide, when a strong base, such as potassic hydrate is added to a solution which contains the chloride of the metal in question, provided that the metal be capable of forming an oxide insoluble in water. For example, if to a solution of cupric chloride, a solution of potassic hydrate be added, the potassium and copper change places, potassic chloride is formed and dissolved, whilst cupric hydrate is precipitated. It is, in fact, an ordinary instance of double decomposition:

$$CuCl_2 + 2KHO \quad \text{give } 2KCl + CuH_2O_2.$$
$$[CuCl_2 + 2K(OH) \text{ give } 2KCl + Cu(OH)_2.]$$

A reaction not less instructive occurs when oxides containing a larger proportion of oxygen than the protoxides are treated with

hydrochloric acid. When, for instance, 1 molecule of ferric oxide, Fe_2O_3, is subjected to its influence, 6 molecules of hydrochloric acid are decomposed, 3 molecules of water are formed, and one of ferric chloride is obtained in solution:

$$6HCl + Fe_2O_3 \text{ give } 3OH_2 + Fe_2Cl_6.$$

It sometimes happens that no chloride corresponding to the oxide exists. There is, for example, no stable tetrachloride of lead: in this case 1 molecule of plumbic dioxide, PbO_2, decomposes 4 molecules of hydrochloric acid; 2 molecules of water and 1 of plumbic chloride are formed, whilst 2 atoms of chlorine are liberated:

$$PbO_2 + 4HCl \text{ give } PbCl_2 + 2OH_2 + Cl_2.$$

The presence of hydrochloric acid and of the soluble chlorides in solution is indicated by the formation of a white, insoluble, curdy precipitate of argentic chloride, when a solution of argentic nitrate is added to the liquid; $NaCl + AgNO_3$ becoming $AgCl + NaNO_3$. This precipitate is soluble in ammonia, but insoluble in nitric acid, although soluble in a solution of sodic thiosulphate, or potassic cyanide. Mercurous nitrate also gives a white precipitate of mercurous chloride (calomel) in solutions of metallic chlorides: $Hg_2(NO_3)_2 + 2NaCl = 2NaNO_3 + Hg_2Cl_2$: $[\mathbf{N}_2O_4(O_2Hg_2)'' + 2NaCl = 2\mathbf{N}O_2(ONa) + \mathbf{Hg}_2Cl_2]$. The precipitate is soluble in chlorine water, insoluble in dilute nitric acid, and is immediately blackened by ammonia. The dry chlorides when heated with potassic dichromate and sulphuric acid yield a red volatile liquid, CrO_2Cl_2, which forms a yellow solution with ammonia: this reaction distinguishes the chlorides from the bromides as the product of the distillation of the latter with the chromate yields a colourless solution with ammonia.

CHAPTER IV.

OXYGEN: O = 16.

Theoretic Density 1·1072; *Observed Density* 1·1056; *Atomic vol.* □; *Molecule in free state* OO □; *Rel. wt.* 16; *Dyad, as in* OH_2.*

(345) *Preparation.*—1. The chemical researches of the philosophers of the last century were especially remarkable on account of the important information which they afforded about the nature

* Formerly the symbol for oxygen was taken as $O = 8$, and the volume occupied by 8 parts by weight of oxygen was employed as the unit of gaseous

of the atmosphere. Indeed, the knowledge thus obtained may be regarded as the starting-point of the brilliant chemical discoveries which have since succeeded each other with such rapidity. These researches have conclusively proved that the air is far from being, as was once supposed, an elementary body; but that, on the contrary, it is a mixture of several substances, some of which are elementary, others compound; the most remarkable and abundant being the elements oxygen and nitrogen.

The most direct proofs of the compound character of the atmosphere are afforded by examining the effects produced upon it by burning bodies. Combustible bodies, as is well known, cannot burn without free access of air. On placing a lighted taper under the receiver of the air-pump and exhausting the air, the flame becomes extinguished. A limited quantity of air will support combustion for but a limited period: a lighted taper floating on water under an inverted bell-glass, the edge of which is plunged beneath the water, soon begins to burn dimly, and at length becomes extinct. But the taper ceases to burn long before the air is all spent; the receiver still contains a large quantity of a gaseous body in which a candle will not burn. The results obtained by burning a candle in a limited portion of air are, however, rather complicated, because the products which are

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volume; but the arguments of Gerhardt and the progress of research required that the number for the atomic weight of oxygen should be doubled, if that of hydrogen was to remain unaltered. Consequently an extensive change became necessary both in notation, and also in the interpretation of chemical phenomena generally.

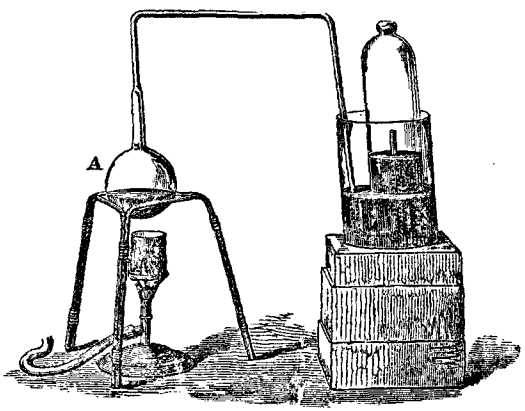
If the atomic weight of oxygen be represented as O = 16, the *molecule* of free oxygen will be OO, with a *molecular* weight = 32, and *molecular* volume [□□]; the atomic weight of hydrogen being H = 1, and the molecule of free hydrogen HH, occupying the same volume as a molecule of oxygen, the molecular weight of water will be $OH_2 = 18$, instead of $HO = 9$. In the various equations by which chemical reactions are represented in this work the molecular volume of compounds will, unless specifically stated to be otherwise, be represented uniformly by 2 volumes.

Oxygen belongs to a class of elements including sulphur, selenium, and tellurium, which may be termed *electro-negative dyads*. Each of these bodies is characterized by the power of uniting with twice its volume of hydrogen, forming a gaseous compound in which the three volumes are condensed into the space of two: one atom of the elements belonging to this group may be said to be equivalent in combination to two atoms of hydrogen or of any of the halogens. The molecule of these elements contains two atoms: *e.g.* SS. or $S_2 = 64$, the molecule of sulphur; $Se_2 = 158{\cdot}2$, the molecule of selenium.

formed by the burning body are partly gaseous, and become mixed with the remaining portion of air. Lavoisier contrived to obviate this inconvenience by acting upon the air with a substance which produced a solid body as the result of the chemical action, so that it left the air unmixed with any gas which rose from the burning body. The material he employed to separate the constituents of the air was metallic mercury, a substance which acts very slowly, and which does not burn in the ordinary sense of the term. The experiment may be performed as follows:

Into the bulb of a flask or retort, A, fig. 278, provided with a neck of considerable length, an ounce or two of metallic mercury is introduced: the neck of the flask is then bent in the manner shown in the figure, and the bent portion plunged into a mercurial bath, so as to leave the open end of the neck projecting above the level of the mercury, into a jar partially filled with atmospheric air. The bulb of this portion of air is then accurately observed, and the temperature and barometric pressure at the time of the observation are recorded. Heat is now applied to the flask, and maintained steadily at a point just below that required to make the mercury boil. If this temperature be continued for three or four consecutive days, the air inclosed both in the flask and in the jar will participate in the action. The mercury in the flask will gradually become covered with red scales, and the air which at first expanded from the action of the heat, and depressed the level of the mercury in the jar, will slowly decrease in bulk, until fresh scales no longer continue to be formed. When this point is reached, the source of heat may be removed, and the remaining air, when cold, will be found to measure about one-fifth less than it did at the commencement. If a portion of this residual air be decanted into another jar, it will be found to be unfit for the support of animal life; a mouse or other small animal introduced into it speedily dies, and the flame of a candle is instantly extinguished. The gas thus obtained is an elementary body, in an almost pure state, termed nitrogen (387), the heated mercury having effected the removal of the oxygen from the air.

FIG. 278.



If the red scales which are formed in the above experiment be introduced into a small glass retort and exposed to a strong heat, they will gradually disappear: drops of mercury will become condensed in the cool part of the retort, and a gas will be

disengaged, which may be collected over water. If the experiment be performed with accuracy, the quantity of the gas obtained will be exactly equal in volume to the bulk absorbed from the air by the mercury. To this gas the name of *Oxygen* (generator of acids, from ὀξὺς, sour, and γεννάω, to produce) has been given. It is an elementary body, and from the abundance in which it occurs, the number and the variety of its compounds, and the necessary part which it performs in the maintenance of life, it must be regarded as the most remarkable and important of the simple bodies.

The above experiment shows that the red scales consist of a compound of mercury and oxygen which is decomposed by heat in the manner represented in the equation:

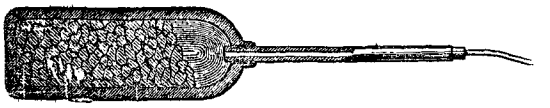
$$2HgO = 2Hg + O_2.$$

There are several other methods of procuring oxygen, the simplest of which consist in the exposure of certain metallic oxides to a high temperature, by which they are made to give up, more or less completely, the oxygen with which the metals were combined.

1.—The original method of Priestley, above described, by which he first isolated pure oxygen, in 1774, by heating the red oxide of mercury to about 400° (752° F.) is of great interest from a historical point of view; there are, however, other modes of procuring oxygen which are more convenient and economical.

2.—For the supply of large quantities of oxygen it is usual to employ the black oxide of manganese, MnO_2, a mineral which, at a red heat, parts with one-third of the oxygen it contains, whilst an oxide of manganese of a reddish-brown colour remains behind; $3MnO_2$, giving $Mn_3O_4 + O_2$. The mineral must be reduced to small fragments of about the size of a pea, and introduced into an iron bottle, fig. 279, to the neck of which an iron pipe is fitted by grinding; the bottle is heated in a furnace, and the gas conveyed to the gas-holder by means of a piece of flexible metallic tubing of suitable length. As the oxide of manganese usually contains water as well as a portion of nitrate and some calcic carbonate, the first effect of heat is to drive off a quantity of steam, mixed with some carbonic anhydride and nitrogen; the latter, however, usually comes off at a later period, and contaminates the oxygen often to the amount of 5 or 6 per cent. When the gas rekindles a glowing match, it may be collected for use. Pure black oxide of manganese furnishes about one-ninth of its weight of oxygen; but as met with in commerce it seldom yields more than half that quantity, a pound giving off about 1400 cubic inches, or a kilogramme about 50 litres of the gas.

FIG. 279.



3.—A supply of very pure oxygen may also be obtained readily by the action of heat upon the salt known as chlorate of potash, or potassic chlorate. About half an ounce, or from 15 to 20 grams of this salt, may be heated over a gas flame or a charcoal fire, in a green glass retort, or in a Florence flask, F (fig. 280), furnished with a cork to which is adapted a wide bent tube for delivering the gas; the salt fuses about 370° (698° F.), and at a temperature a little above this emits a large quantity of gas, which may be collected in jars over water in the pneumatic trough, or if not wanted for immediate use, may be stored up in a gas-holder (39). If a jar of the gas be closed with a glass plate it may be inverted, as at A, fig. 281, and its power of supporting combustion tested by a taper, as shown at B. The oxygen furnished by the chlorate amounts to more than one-third of the weight of the salt used; 1 ounce or 28·3 grams of the crystals should yield about 7·75 litres, or nearly $1\frac{3}{4}$ gallons of the gas. Potassic chlorate, $KClO_3$, when heated sufficiently, is decomposed, and gives up all its oxygen in the gaseous form, whilst the chlorine and potassium unite to form potassic chloride, the white salt, which remains in the retort when the operation is over. The change may be thus represented in symbols: $2KClO_3 = 2KCl + 3O_2$: $\left[2 \left\{ \begin{matrix} OCl \\ O(OK) \end{matrix} \right. = 2KCl + 3O_2 \right]$: this decomposition of potassic chlorate, however, takes place in two stages, in the first of which only one-third of the total quantity of oxygen present in the salt is given off as represented in the following equations:

FIG. 280.

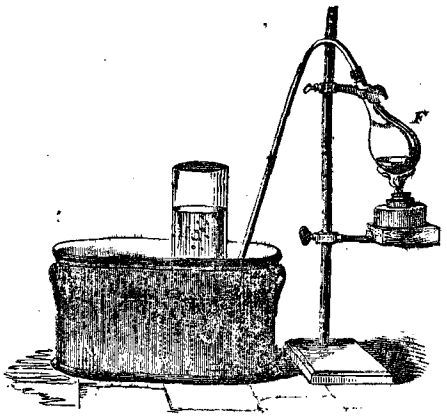
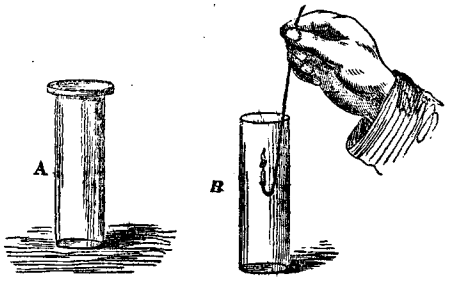


FIG. 281.



$$\underset{\text{Potassic chlorate.}}{2KClO_3} = \underset{\text{Potassic chlorite.}}{KClO_2} + \underset{\text{Potassic perchlorate.}}{KClO_4} \quad \text{and} \quad \underset{\text{Potassic chlorite.}}{KClO_2} = \underset{\text{Potassic chloride.}}{KCl} + \underset{\text{Oxygen.}}{O_2}.$$

In the second stage, which requires a much higher temperature, the potassic perchlorate is decomposed: $KClO_4 = KCl + 2O_2$.

4.—When the quantities of chlorate employed are rather large, the heat required to complete the decomposition is apt to soften the glass of the flask in which the operation is performed. It has, however, been found that many metallic oxides, if mixed in fine powder with the pulverized chlorate in a proportion of not less than one part to ten of the salt, cause the decomposition to take place at a much lower temperature, ranging between 232° and 260° (450° and 500° F.),

although such oxides do not appear to undergo any chemical change during the operation. It is therefore convenient in practice to mix the potassic chlorate with about a fourth of its weight of oxide of copper, black oxide of manganese, or ferric oxide, that has been previously heated to redness and allowed to cool. The gas which is obtained in this way always contains traces of chlorine, and the heat must be carefully regulated, as at a particular point the oxygen is disengaged with very great rapidity, so that it is necessary to employ a wide delivery tube.

Oxygen may be obtained from various other substances, but those already mentioned are the best, and are the materials most frequently employed. Red lead, and the peroxides of most of the metals, such as those of silver and lead, as well as the nitrates of potassium, sodium, and barium, furnish the gas when strongly heated; it may also be obtained by heating chloride of lime or bleaching powder, or by the action of heat on a mixture of chlorine and steam, or by passing chlorine into a solution of potassic or sodic hydrate containing a small quantity of cobaltic hydrate in suspension; sulphuric acid, many sulphates, and baric dioxide likewise yield oxygen when submitted to a high temperature; powdered oxide of manganese or potassic dichromate, $K_2CrO_4.CrO_3$, when heated with twice its weight of concentrated sulphuric acid in a glass retort also evolves oxygen.

5.—When potassic dichromate (bichromate of potash) and sulphuric acid are heated together they undergo decomposition—oxygen, hydric potassic sulphate, and chromic sulphate being produced. This change may be represented in the following manner:

$$\underset{\text{Potass. dichrom.}}{2K_2Cr_2O_7} + \underset{\text{Sulph. acid.}}{10H_2SO_4} = \underset{\text{Hydric potass. sulph.}}{4KHSO_4} + \underset{\text{Chrom. sulph.}}{2(Cr_2 3SO_4)} + \underset{\text{Water.}}{8OH_2} + \underset{\text{Oxygen.}}{3O_2}.$$

$$\left[2\left\{\begin{matrix}\mathbf{Cr}O_2(OK)\\ O\\ \mathbf{Cr}O_2(OK)\end{matrix}\right. + 10\mathbf{S}O_2(OH)_2 = 4\mathbf{S}O_2(OH)(OK) + 2\mathbf{S}_3O_6(O_6Cr_2)^{vi} + 8OH_2 + 3O_2.\right]$$

Part of the sulphuric acid is employed in displacing the chromic acid from the dichromate, forming hydric potassic sulphate, whilst the liberated chromic acid, in presence of the excess of sulphuric acid, gives up half its oxygen, and becomes converted into chromic sulphate, with elimination of water.

6.—If a stream of chlorine be passed through boiling water and the resulting mixture of steam and chlorine transmitted through a porcelain tube filled with fragments of pumice stone and heated to bright redness, hydrochloric acid is produced and oxygen liberated, $2OH_2 + 2Cl_2 = 4HCl + O_2$. The oxygen is freed from hydrochloric acid and any excess of chlorine that may be present by washing it with a solution of sodic hydrate.

7.—When a current of chlorine is passed into a hot solution of sodic or potassic hydrate, to which a few drops of a solution of cobaltous chloride or nitrate have been added, the chlorine is at the first moments absorbed, converting the precipitated cobaltous hydrate into cobaltic hydrate, $Co_2(OH)_6$, and subsequently the liquid effervesces, evolving pure oxygen. The cobaltic hydrate undergoes no change, and may be used indefinitely, whilst the sodic hydrate is converted into chloride. Another modification of this process consists in heating a mixture of "chloride of lime" and water, to which a small quantity of a solution of a cobaltous

or cupric salt has been added, taking the precaution to place a few pieces of paraffin in the flask: this melts, forming a layer on the surface of the liquid, and thus prevents the frothing which would otherwise take place.

8.—When oxygen is required in large quantities, as in metallurgic operations, Deville and Debray recommend the decomposition of sulphuric acid by heat as the cheapest source of the gas. A tubulated earthenware retort is charged with fragments of fire-brick, an iron tube sufficiently long to reach to the bottom of the retort is luted into the tubulure, and when the retort is at a full red heat, the acid is allowed to pass in, drop by drop, through a bent funnel. In this operation the sulphuric acid is decomposed into sulphurous anhydride, oxygen, and water, as represented by the following equation:

$$\underset{\text{Sulphuric acid.}}{2H_2SO_4} = 2OH_2 + \underset{\text{Sulphurous anhydride.}}{2SO_2} + O_2.$$

$$[2SO_2(OH)_2 = 2OH_2 + 2SO_2 + O_2.]$$

The volatilized products are passed through a small spiral condenser to condense the water and undecomposed acid, whilst the sulphurous anhydride is removed by subsequent washing with water, and the oxygen is collected in the usual manner.

9.—Dried zincic sulphate also readily yields oxygen and sulphurous anhydride on the application of a full red heat, whilst zincic oxide remains in the retort:

$$\underset{\text{Zincic sulph.}}{2ZnSO_4} = \underset{\text{Zincic oxide.}}{2ZnO} + 2SO_2 + O_2.$$

$$[2SO_2(O_2Zn) = 2ZnO + 2SO_2 + O_2.]$$

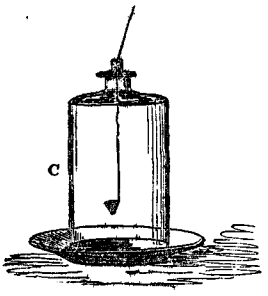
10.—Baric dioxide, BaO_2, was also proposed by Boussingault as a source of oxygen. He hoped to convert baryta alternately into the dioxide, by heating it to a dull redness in a current of air, and then to decompose this dioxide by a still more elevated temperature, and thus be able to employ the same quantity of baryta an indefinite number of times to extract oxygen from the atmosphere. Hitherto the difficulties attending the use of this method have prevented its application in the arts.

11.—Potassic permanganate, K_2MnO_4, is decomposed, and gives off oxygen on being heated in a current of steam, leaving behind potassic hydrate and an oxide of manganese; this residue, when heated with access of dry air, absorbs oxygen, and gives it up again when heated in a current of steam, so that the product may be used over and over again to obtain oxygen from the atmosphere (Tessié du Motay, *Ding. pol. Jour.*, 1867, clxxxvi. 230). This process has been applied to the preparation of oxygen on the large scale, a detailed account of which by Pourcel, will be found in the *Memoires de la Société des Ingénieurs Civils*, 1873.

Properties.—Oxygen possesses extremely powerful chemical attractions for other elementary substances; only one (fluorine) being known with which it does not combine. Owing to the great energy with which many of these combinations take place, oxygen possesses the power of supporting combustion in an eminent degree. If a splinter of wood with a glowing spark on any part of it be plunged into the gas, the wood will instantly burst into flame, and burn with extraordinary brilliancy. Many bodies which burn tranquilly in air often deflagrate with violence in oxygen.

Phosphorus burns in it with a brilliancy which is painful to the eye; in like manner, sulphur and charcoal burn vigorously in the gas, as do also many metals; a piece of potassium the size of a pea, if placed in a small copper spoon, c, fig. 282, and heated strongly by a spirit lamp, bursts into flame when plunged into the gas. A piece of watch spring or thin steel wire will burn in oxygen with brilliant scintillations, if some German tinder be fastened to the wire and ignited previously to introducing it into the gas; the use of the tinder being to start the combustion. Zinc foil, also, tipped with sulphur and kindled, burns in oxygen with an intense bluish white light.

FIG. 282.



In these cases the oxygen combines with the burning body, producing in each instance a new substance, quite different in properties both from the oxygen and from the body burned.

Oxygen is essential to the support of animal life, and on this account was termed *vital air* by the older chemists. A small animal will live in a confined space filled with oxygen for a longer period than in an equal bulk of air; but the gas cannot be breathed undiluted with impunity for any considerable time: Dr. B. W. Richardson found that a rabbit might be kept alive in a stream of pure oxygen at the temperature of 23°·9 (75° F.) for three weeks, during which time it ate voraciously, but, nevertheless, became so emaciated from inability to eat sufficient to supply the waste, that it was necessary to discontinue the experiment. At the temperature of 7°·2 (45° F.), the rabbit was speedily narcotized, and died unless removed. When the oxygen was cooled by a freezing mixture, the narcotism was so perfect and rapid, that operations could be performed on the animal. The gas which has been once breathed, rapidly produces narcotism and death, even after washing with potassic hydrate and sulphuric acid; and, although no carbonic anhydride could be detected in the gas, yet it produced the same effects on the rabbits at all temperatures. The passage of a few electric sparks through the oxygen restored it to its original condition and removed the narcotic property.

Oxygen, like air, is destitute of colour, taste, and smell. Of all known substances it exerts the smallest refracting power upon the rays of light. All attempts hitherto made to reduce it to the liquid form by the combined application of pressure and cold have proved fruitless. It has been ascertained that oxygen possesses feeble magnetic properties, similar to those of iron, and like this substance its susceptibility to magnetization is diminished,

or even temporarily suspended, by a sufficient elevation of temperature (325). It is heavier than the atmosphere, its specific gravity, according to Regnault, being 1·10563; 1 litre at 0° C., and 760$^{mm.}$ pressure, weighing 1·4298 grams; or 100 cubic inches at 60° F. and 30 inches Bar., weighing 34·206 grains; it is only slightly soluble in water, which takes up about $\frac{1}{25}$ of its bulk, at 0° (32° F), and $\frac{1}{33}$ at 15° (59° F.); 100 volumes of water, according to Bunsen, dissolving 4·11 vols. at 0° (32° F.) and 2·99 at 15° (59° F.). The solubility of oxygen in alcohol between 0° and 24° (32° and 75°·2 F.) is constant, 100 volumes dissolving 2·8397 of the gas.

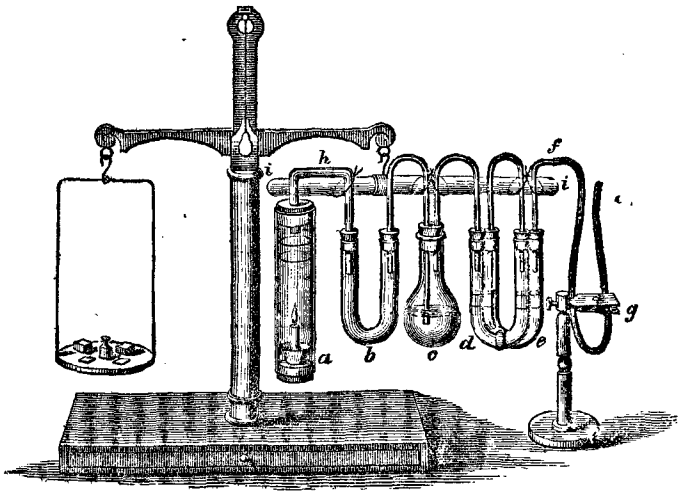
(346) **Nature of Combustion.**—The distinguishing feature of oxygen is its remarkable power of supporting combustion. Whenever any rapid chemical action attended with production of light and heat takes place, *combustion* is said to occur. In order to commence this action it is generally necessary to apply heat; afterwards the heat which is liberated during the process is more than sufficient to carry it on, and the act of combination proceeds with increasing rapidity, until it attains a maximum under the conditions of experiment. A stick of charcoal may be kept in oxygen at ordinary temperatures for years without entering into combination with the gas, but the smallest spark upon the surface of the charcoal will suffice to determine its immediate and vivid combustion.

It must be borne in mind that there is no destruction of matter or loss of weight, either during combustion, or in any other case of chemical action, although the combustible or body which is burned may undergo such a complete change of form as even to disappear from our sight. A candle in burning seems to be completely destroyed; and when the combustion is over, an insignificant trace of ash from the wick is all that remains to the eye. It is, however, easy to show that there is no actual destruction of its components in this operation, but that the constituents of the candle in burning have combined with a certain proportion of oxygen, and that the aëriform compounds, carbonic anhydride and aqueous vapour, which are the result of the combustion, although invisible, really weigh more than the original candle; the gain in weight representing the quantity of oxygen which has produced the chemical change by its combination with the materials of the candle.

The following apparatus affords a convenient method of showing this. A cork, perforated with three or four holes to admit air, is inserted into the lower end of a glass tube, *a*, fig. 283, which may be an ordinary Argand lamp glass;

on this rests a cup to catch any drops of wax which may fall from the small piece of candle fixed into it. The upper end of the cylinder is in connexion with the rest of the apparatus by the bent glass tube *h* passing through a tightly fitting cork. The U-tube *b* is empty, the flask *c* half filled with lime-water, and the other two U-tubes *d* and *e* are filled with fragments of soda, lime, or potassic hydrate, to retain any aqueous vapour or carbonic anhydride which may have escaped through *b* and *c*; these different parts of the apparatus being firmly fixed to a piece of wood *i*, *i*, by which they may be suspended from

FIG. 283.



the arm of the balance. The exit of the last tube *f* is connected with an aspirator or water air-pump by means of two lengths of flexible caoutchouc tubing joined by a piece of glass tube *g* rigidly fixed in a clamp, thus preventing the communication of any motion to the apparatus attached to the balance. The apparatus having been carefully counterpoised, the candle is taken out, lighted, and replaced, the aspirator being set in action at the same time. Water condenses in *b*, and the lime-water in *c* becomes turbid from the carbonic anhydride combining with the lime and forming insoluble calcic carbonate, at the same time the arm of the balance to which the apparatus is attached gradually descends, showing that the products of combustion of the candle weigh more than the body burned.

The water air-pump mentioned above, is an instrument constructed on the same principle as Sprengel's air-pump (30 *a*), water being used instead of mercury. By its means a rapid current of air may be drawn through an apparatus, and with a fall tube of about 36 feet, a near approach to a vacuum can be obtained. The instrument is known as Bunsen's pump.

At the ordinary temperature of the atmosphere, oxygen frequently enters so slowly into combination that the heat disengaged is not perceptible, as when a bar of iron is gradually rusting

in the air.* In other instances, where the process is more rapid, the heat accumulates, and sometimes rises high enough to cause the materials to burst into flame, producing what are called cases of spontaneous combustion. Charcoal that has been reduced to fine powder as a preliminary to the manufacture of gunpowder, and which offers a large surface to the air, occasionally exhibits this phenomenon; and it is still more often manifested when tow that has been used for wiping machinery lubricated with oil is laid aside in heaps. The oil, when spread over so large a surface, absorbs oxygen rapidly, and the temperature goes on rising until the mass bursts into flame.

It has been observed that the oxidation of the metals takes place much more rapidly in a moist than in a dry atmosphere. A bar of polished iron will remain unchanged for any length of time in dry air, but if moisture be present, it quickly becomes rusty. In the case of iron, the oxidation continues to spread through the entire mass of the metal; but in other instances, as with lead, zinc, and some other metals, a superficial coating of oxide is formed, which adheres firmly to the surface, and protects the metal beneath from further change.

When the oxygen is mixed with a gas which does not act on it chemically, as with the nitrogen of the atmosphere, the tem-

* When considerable masses of iron are allowed to rust, a distinct elevation of temperature is often perceived. This is seen when a heap of iron turnings of from 11 to 22 lb. (5 to 10 kilog.) is moistened with water and exposed to the air; and a curious illustration of the fact was afforded during the manufacture of the Mediterranean electric cable. The copper conducting wire of this cable was coated with gutta-percha, this was covered with a serving of tar and hemp, and the whole enclosed in a strong casing of iron wire. The cable as it was manufactured was coiled in tanks filled with water. These tanks leaked, and the water was in consequence drawn off, leaving a quantity of cable, about 163 nautical miles in length, coiled into a mass about 30 feet or 9 metres in diameter, with an eye or central space of 6 feet (rather less than 2 metres); the height of the coil was about 8 feet (2·5 metres). Rapid oxidation took place, and the temperature at the centre of the coil, nearly 3 feet (0·9 metre) from the bottom, rose in 4 days from 19° to 26° (66° to 79° F.), although the temperature of the air did not exceed 19° (66° F.) during the period, and was as low as 15° (59° F.) part of the time. In other parts of the mass the heat rose so high as to cause the water to evaporate sufficiently rapidly to produce a visible cloud of vapour, and to give rise to apprehensions that the insulating power of the cable would be destroyed by the softening of the gutta-percha. No doubt the rise of temperature would have been still greater had it not been checked by the affusion of cold water; but the oxidation and the heating were renewed when the affusion was discontinued. The oxidation occurred only on the external surface of the iron wires, the portion in contact with the tarred hemp remaining perfectly bright.

perature which is produced by combustion is lower, and the operation proceeds more slowly, because fewer particles of oxygen come in contact with the burning body in a given time, and part of the heat developed is employed in raising the temperature of the inert gas. The activity of the combustion is greatly augmented by increasing the number of particles of oxygen which are brought in a given time into contact with the combustible, as well as by carrying away the gaseous products of combustion which are incapable of combining with the fuel, and which, if suffered to accumulate, would cut off the supply of fresh oxygen; in this way, the action of the smith's bellows and the blowing machine of the blast furnace may be explained. The influence of a long chimney in producing a powerful heat in the furnace at its base is similar; whilst the effect of diminishing the supply of air by closing the damper, or shutting the door of the ash-pit, is seen in the diminished temperature and reduced consumption of fuel which occur under such circumstances.

It is, however, important to remark that the quantity of heat emitted during the combination of a given quantity of oxygen is definite, and varies only with the chemical nature of the burning body, being quite independent of the rate at which the combustion is effected (199 *et seq.*).

The effect of respiration in animals, during which the oxygen of the air is brought into contact with the blood through the agency of the lungs, is analogous to combustion, and is accompanied by development of heat; oxidation occurs, carbonic anhydride is eliminated and passes off with the expired air, and at the same time the colour of the blood is changed from a dusky purple to bright crimson.

All bodies, with reference to combustion, may be conventionally arranged under one of three classes. The first class consists of bodies which, like oxygen, allow other substances to burn in them freely, but which cannot themselves, in ordinary language, be set on fire; these are termed *supporters of combustion.* The second class consists of bodies which, like charcoal, actually burn when sufficiently heated in a gas belonging to the first class: these substances are termed *combustibles.* It must, however, be remembered that the terms combustible and supporter of combustion are merely relative, for although under ordinary circumstances hydrogen is a combustible, and oxygen and chlorine supporters of combustion, yet these two last-mentioned gases are quite capable of burning when surrounded by an atmosphere of hydrogen. The third class embraces such bodies as will neither burn

themselves nor support the combustion of others: they may be made red hot, but do not burn; sand, iron-rust, and earthy bodies in general, afford examples of this kind; they are for the most part compounds that may have at some time or other been produced by combustion; that is, they are bodies that have been already burned, and are no longer fitted to undergo this change.

(347) **Oxides.**—The compounds which oxygen forms with other elements are in chemical language termed *oxides*, and a body which has combined with oxygen is said to have become *oxidized*. The number and variety of these compounds are very great, for oxygen is the most widely diffused and abundant of the elements. It constitutes about a fifth in bulk of the atmosphere; it forms eight-ninths of all the water on the globe, and is not less extensively met with amongst the solid constituents of the earth: chalk, limestone, and marble—silica in all its varieties of sand, flint, quartz, rock-crystal, &c.—as well as the various kinds of clay, each contains about half its weight of oxygen. It is also generally diffused in the forms of animal and vegetable life; being indeed absolutely essential to the maintenance of the vital functions in both.

It is remarkable that amongst the various compounds formed by oxygen, two classes exist which are in chemical properties directly opposed to each other. Many substances, like phosphorus, by their combination with oxygen, yield a compound which is freely soluble in water, producing a liquid which has a sour, burning taste, and turns many vegetable blue colours, such as an infusion of litmus or purple cabbage, to a bright red; which, in short, possesses the characters we ordinarily designate as *acid*. All the non-metallic elements, with the exception of hydrogen and fluorine, form one or more compounds with oxygen, which, when united with the elements of water, yield acids, and in many cases intensely powerful acids. Many of the metals, however, by their union with oxygen, give rise to bodies possessing properties of an opposite kind, and which have been termed *bases*. Potassium, for example, when burned in oxygen, furnishes a white alkaline substance, which is dissolved rapidly by water, and produces a colourless liquid, of a soapy, disagreeable taste, and a peculiar odour: it has a caustic action on the skin, restores the blue colour to litmus which has been reddened by an acid, and completely neutralizes the strongest acids. Other metals form oxides which, although not soluble in water, preserve their basic character, and neutralize the acid perfectly. Ferrous oxide, for instance, is

soluble in sulphuric acid, and forms with it a crystallizable salt, whilst water is set free. It is found in almost all cases that when an element combines with oxygen to form an oxide which by addition of water produces an acid, it unites with a larger number of atoms of oxygen than when a base is the result of the combination.

Intermediate between the acid and the basic oxides is a third class of oxides, which are indisposed to enter into combination with either acids or bases. The black oxide of manganese, MnO_2, or, $MnO.MnO_3$, the magnetic oxide of iron, $FeO.Fe_2O_3$, and red lead, $2PbO.PbO_2$, may be mentioned as instances of this kind: such oxides are often produced by the union of two other oxides with each other. These indifferent oxides are sometimes termed *saline* oxides, from their analogy to salts in composition.

Independently of its power of supporting animal life and combustion, oxygen may be distinguished by direct tests. It is insoluble in a solution of potash, but if a little pyrogallic acid be added to the alkaline liquid, the gas is rapidly absorbed, and the solution becomes of a deep brown colour. A mixture of nitric oxide with any gas containing uncombined oxygen immediately becomes of a reddish-brown colour, owing to the formation of red fumes of peroxide of nitrogen (405): and a colourless solution of cuprous oxide in ammonia is instantly rendered blue by the action of uncombined oxygen.

(348) **OZONE**: O_3 or $\begin{matrix} O \\ / \quad \backslash \\ O—O \end{matrix}$.—When a succession of electric sparks is transmitted through atmospheric air or dry oxygen, a peculiar odour is perceived, which has by some been compared to that of diluted chlorine. To the body which produces it, Schönbein gave the name of *ozone* (from ὄζω, to emit an odour) in allusion to its strong and peculiar odour. Opinions upon the cause of this odour were long divided; but the observations of several accurate experimentalists indicate that it is owing to a modification produced in oxygen itself, by which it is made to assume a more active condition. One of the easiest methods of exhibiting the production of ozone consists in passing a current of dry oxygen through a tube into which a pair of platinum wires is sealed, with the points at a little distance apart: on connecting one of the wires with the prime conductor of an electrical machine in good action, whilst the other wire is in conducting communication with the earth, the characteristic odour of ozone is immediately developed in the issuing gas; but notwithstanding the

powerful odour thus produced, only a minute portion of the oxygen undergoes this change. Andrews and Tait (*Phil. Trans.* 1860) have shown that in order to produce the maximum effect in electrifying oxygen, it is necessary to transmit the discharge *silently*. By operating in sealed tubes upon pure and dry oxygen, they succeeded, when great care was taken to prevent the passage of sparks, in converting a considerable portion of the gas into ozone. Ozone is much denser than oxygen itself; by a continuous electrical discharge maintained for many hours, they effected a contraction in bulk of the gas amounting to one-twelfth of the entire volume operated on; and on heating the gas to 288° (550° F.) the ozone disappeared, whilst the oxygen resumed its original volume. The passage of the electric *spark* immediately destroys a large proportion of the ozone which has been previously produced.

One of the most convenient forms of apparatus for the preparation of ozone is that devised by Siemens, consisting of a long glass tube coated on the interior with tin foil, over which passes a slightly larger tube covered with tin foil on its outer surface. On connecting the inner and outer coatings with the terminal wires of an induction coil, and passing a current of pure dry oxygen through the annular space between the two tubes, this gas is acted upon by the silent discharge, and a comparatively large proportion converted into ozone. Wills has recently proposed to replace the inner tube by a brass box tinned on the outside, and having a current of ice cold water passing through it in order to prevent the heating of the apparatus. By employing an apparatus very similar to Siemens, but using electricity of high tension from a Holz machine instead of from any induction coil, and passing oxygen through it at the rate of ·87 to ·44 litres per hour, Giannetti and Volta (*Gaz. Chim. Ital.* v. 489) found the gas to contain from 36 to 38 milligrams of ozone per litre.

When dilute sulphuric acid, or a solution of the sulphates, chromates, phosphates, and several other salts of the alkali-metals, is decomposed electrolytically by the voltaic battery, employing plates of platinum or gold as electrodes, the oxygen that is evolved contains ozone; the quantity of this is largely increased if the electrolysis of the dilute sulphuric acid be conducted at a very low temperature. The experiments of Andrews (*Phil. Trans.* 1855 and 1860) have shown the identity of the ozone obtained by the electricity of the machine, with that produced by voltaic action, as well as with that obtained by the oxidation of phosphorus; and these conclusions have been confirmed by Soret and by Von Babo (*Ann. Chem. Pharm. Sup.*, 1863, ii. 266), in opposition to Baumert, who maintained (*Pog. Ann.*, 1853, lxxxix. 38) that electrolytic ozone contains a peculiar peroxide of hydrogen, as Schönbein himself at one time supposed.

Ozone may also be obtained without the aid of electricity

Houzeau states that the oxygen evolved from baric dioxide, BaO_2, by the addition of oil of vitriol, contains ozone; it has a powerful odour, and he found that it oxidizes ammonia, and kindles the less inflammable variety of phosphuretted hydrogen; after it has been heated it no longer possesses these properties. The gas evolved by the action of sulphuric acid on potassic permanganate behaves similarly. Later researches have, however, rendered it probable that these properties are due to the formation of peroxide of hydrogen in small quantity, and to its suspension in the oxygen as it escapes.*

If a stick of phosphorus, moistened with a few drops of water, be placed in a bottle of atmospheric air, at a temperature of from 15° to 21° (60° to 70° F.), the slow oxidation of the phosphorus is attended with the production of ozone: in an hour or two this attains its maximum. If the phosphorus be not then removed, the ozone disappears by degrees, owing to its combination with the phosphorus. No ozone is formed if the air be perfectly dry, neither is dry oxygen ozonized by phosphorus. It appears also that ozone is formed in other slow oxidations, such as that of ether, benzene, and oil of turpentine; although in the case of oil of turpentine Kingzett (*Journ. Chem. Soc.*, 1874, xxvii. 511) considers the effects produced to be due to hydrated protoxide of turpentine, $C_{10}H_{16}O.OH_2$, and not to ozone or hydric peroxide. Schönbein seems to have proved that in all such cases the formation of ozone is accompanied by that of peroxide of hydrogen, H_2O_2, a fact which is true also of electrolytic ozone.† Ozone is formed in small quantity when a mixture of oxygen and hydrogen is exploded.

It was noticed by Lender that in the concentration of the water of saline springs by graduation, the air in the immediate neighbourhood of the columns

* The reader is referred for Schönbein's speculations upon the existence of two opposite forms of oxygen, *ozone* and *antozone*, to the *Phil. Mag.* for 1858. They are ingenious, but although the existence of two oppositely polarized forms had previously been rendered probable by the experiments of Brodie and others, it is not in accordance with analogy, that ozone should be the isolated form of one of these bodies. A mixture of a solution of potassic permanganate with one of peroxide of hydrogen evolves oxygen, whilst hydrated peroxide of manganese is precipitated; and in like manner a solution of chromic acid acidulated with sulphuric acid gives off oxygen on the addition of peroxide of hydrogen, whilst green chromic sulphate is produced. Hence it has been supposed that the oxygen in the permanganic or chromic acid is in an opposite polar condition to the second atom of oxygen in the peroxide of hydrogen; the tendency to union between these two supposed oppositely polar forms of oxygen is conceived to be the cause of the decomposition, and the result of their union is the gaseous oxygen which escapes. (See also Brodie, *Phil. Trans.* 1850 and 1862) Von Babo's experiments tend to show that Schönbein's so-called antozone is peroxide of hydrogen.

† If a clean glass rod heated to about 260° (500° F.), be plunged into a jar containing a few drops of ether, the vapour undergoes slow oxidation, and ozone seems to be formed: the vapours turn starch paper, moistened with a solution of potassic iodide, blue; the residual ether contains peroxide of hydrogen, and if agitated with a few drops of a solution of potassic chromate acidulated with a little sulphuric acid, a blue solution of perchromic acid in the ether is obtained.

gave the ozone reaction, and Gorup-Besanez subsequently found that the quantity of ozone produced by the spray of water issuing under pressure was greater the more rapid the evaporation. This has been confirmed by other observers, and Bellucci (*Gaz. Chim. Ital.*, 1876, vi., 88) has recently found that the presence of ozone is very marked in the air in the neighbourhood of cascades. From this it would appear that ozone is generally produced where water undergoes pulverization, or is converted into finely divided spray, whether this is effected by a cascade, a torrent rushing over rocks, the surf on the sea-shore, or the rolling of the waves in the open ocean, for it is noteworthy that the air over the surface of the ocean is richer in ozone than that collected on land.

Properties.—Ozone is very slightly soluble in cold water, but the solution possesses the characteristic properties and odour of ozone. It is gradually converted into ordinary oxygen in contact with water, but this transformation takes place very slowly at low temperatures. Carius (*Ann. Chem. Pharm.*, 1874, clxxiv. 1) states that the co-efficient of absorption for ozone at 1° (33°·8 F.) and under 760 mm. pressure is 0·834; it is also freely absorbed by a solution of potassic iodide. Air charged with ozone exerts an irritating action upon the respiratory organs. Ozone possesses considerable bleaching powers, and converts indigo blue into isatin: it acts rapidly as a powerful oxidizing agent, and corrodes most organic matters, such as cork or caoutchouc; paraffin, however, is not acted on, and therefore forms an excellent means for connecting the different parts of the apparatus used in experimenting with ozone; iron, copper, and silver, when moistened, absorb it rapidly, and become converted on their surface into oxides: silver even becomes a peroxide, although this metal does not enter into direct combination with ordinary oxygen either when moist or dry. When the ozone and the metals are perfectly dry, little or no absorption occurs. Dry mercury, however, as well as dry iodine, immediately removes ozone; the mercury becoming tarnished and adhering to glass surfaces. It is remarkable that no contraction follows the absorption of ozone by these agents; this point was carefully and minutely observed by Andrews and Tait. Hence it seems to be probable that the ozone is resolved into a quantity of ordinary oxygen, equal in bulk to itself, which is liberated at the moment that the other portion enters into combination with the iodine; in this way it would appear that three volumes of oxygen become condensed into two; one volume being fixed, whilst two volumes are liberated on the decomposition of ozone by a metal. The experiments of Soret on the absorption of ozone by oil of turpentine, and on its rate of diffusion, favour this supposition, which has been confirmed by the recent investigations of Sir Benjamin Brodie (*Phil. Trans.*, 1872, 435). Ozone displaces iodine from

its combinations with the metals, setting the iodine at liberty; indeed, this reaction takes place so easily, that it furnishes the readiest and most delicate method of detecting the presence of traces of ozone in the air; a slip of paper moistened with starch paste and potassic iodide, when exposed to a gas containing the smallest admixture of ozone, becomes blue from the action of the liberated iodine on the starch forming the characteristic blue compound of iodine and starch. Indeed, pure oxygen contained in a tube inverted over a solution of potassic iodide is entirely absorbed by the liquid, if the gas be subjected to the passage of a discharge of electricity through it for a sufficient length of time, potassic hydrate being formed by the absorption of oxygen, whilst iodine is set free: $4KI + 2OH_2 + O_2 = 4KHO + 2I_2$. If the experiment be prolonged, potassic iodate, peroxide of hydrogen, and peroxide of potassium are formed. Paper soaked in a solution of manganous sulphate, $MnSO_4$, likewise shows the presence of ozone by turning brown, owing to the manganese in the sulphate absorbing oxygen, and becoming converted into the insoluble hydrated peroxide, whilst sulphuric acid is set free. If the paper be stained black with plumbic sulphide, PbS, this stain will gradually disappear; the compound absorbing the ozone, and becoming oxidized to plumbic sulphate, $PbSO_4$, which is white. One of the most singular circumstances connected with ozone is the effect produced by elevation of temperature, for when heated a little above 100° (212° F.), it is slowly converted into ordinary oxygen, and the change is instantaneous at the temperature of 237° (458°·6 F.). By placing the flame of a spirit-lamp so as to heat a part of the tube through which the electrified oxygen escapes, all signs of ozone disappear. Ozonized air is also deozonized by transmission over cold manganic dioxide, argentic dioxide, or plumbic dioxide.

If a piece of paper soaked in a mixture of starch and potassic iodide be exposed in the open air for five to ten minutes, it often acquires a blue tint, the intensity of which varies on different days; sometimes, particularly in damp or foggy weather, no change is produced by such exposure. These effects are seldom seen in towns, but generally in the open country, or on the sea coast, especially when the wind blows off the sea. They are plausibly supposed to be owing to the presence of traces of ozone in the atmosphere, and theorists are not wanting who believe they have traced the prevalence of cholera and other epidemics to the unusual absence of ozone in the air during lengthened periods. Iodine may, however, be liberated from

potassic iodide by nitrous acid, by chlorine, and by various agents besides ozone, so that this reaction, although a very sensitive one for ozone, is by no means characteristic of its presence; the existence in the atmosphere of some agent more powerful in its oxidizing action than ordinary oxygen is certain, but that this is ozone cannot be said to have been unequivocally proved. Schönbein, in order to obtain some idea of the proportion of the agent which produces this effect, prepares the test-paper of a definite strength, by dissolving 1 part of pure potassic iodide free from iodate in 200 parts of distilled water, which is thickened by heating it with 10 parts of white starch: this is then spread upon slips of unsized paper, which are dried at the ordinary temperature and preserved in a stoppered bottle away from the light.

It was at one time believed that the green parts of plants evolved ozone under the influence of the solar rays, but Cloez and also Bellucci (*Compt. Rend.*, 1874, lxxviii. 362) have conclusively proved that this is not the case, the change in the iodized test-paper being due to the combined effects of moisture, oxygen, and light upon it.

CHAPTER V.

WATER.—PEROXIDE OF HYDROGEN.

WATER: $OH_2 = 18$; *Atomic and Mol. Vol. of Vapour* [ ]; *Rel. wt.* 9; *Density as Vapour, Theoretic,* 0·6228; *Observed,* 0·622, *as Liquid* 1·000, *as Ice* 0·91674 (Bunsen).

(349) On the uses of water, it is almost needless to enlarge, for they are universally felt and appreciated. In each of its three physical conditions, the blessings which it confers upon man are inestimable. As ice, it furnishes in northern lands for months together, a solid bridge of communication between distant places; in the liquid condition, it is absolutely necessary to the existence of vegetable and animal life; in this shape, too, it furnishes to man a continual source of power in the flow of streams and rivers; it supplies one of the most convenient channels of communication between places widely separated, and further, it is the storehouse of countless myriads of creatures fitted for use as food: in the state of vapour, as applied in the steam-engine, it has furnished a power which has in later years done more than any other physical agent to advance civilization, to economise time, and to ameliorate the social condition of man. Nor must we pass over the important effects produced by the opacity to heat

of the aqueous vapour contained in the air, and which acts as a sort of screen in preventing radiation from the earth. Although the night may be cloudless and perfectly clear, if the atmosphere be charged with aqueous vapour it will entirely intercept the obscure heat radiated from the earth. In each and all of these points, if rightly considered, we must perceive the entire adaptation of this wonderful compound to the ends which it was designed by the Creator to fulfil.

Glancing at the physical condition of our planet, we cannot fail to be impressed with the important effects produced by the movements of water at periods anterior to the existence of man, as well as in more recent times. To such causes we must refer the formation of sedimentary rocks, and their arrangement in successive strata upon the surface of the earth: even now, observation shows that denudation is proceeding at some points, elevation and filling up of hollows at others; whilst the accumulation of drift, and a variety of other extensive geological changes must be traced to the same ever-acting and widely operating agency.

It may further be observed that there is no form of matter which contributes so largely as water to the beauty and variety of the globe that we inhabit. In its solid state, we are familiar with it in the form of huge glaciers, of blocks of ice, of sleet and hail, of hoar-frost fringing every shrub and blade of grass, or of snow protecting the tender plant, as with a fleecy mantle, from the piercing frosts of winter. The rare but splendid spectacle of mock suns, or parhelia, are due to the refractive power of floating spiculæ of ice upon the sun's rays. In its liquid condition, as rain or dew, it bathes the soil; and the personal experience of all will testify to the charm which the waterfall, the rivulet, the stream or the lake, adds to the beauty of the landscape; whilst few can behold unmoved the unbounded expanse of ocean, which, whether motionless, or heaving with the gently undulating tide, or when lashed into foam by the storm that sweeps over its surface, seems to remind man of his own insignificance, and of the power of Him who alone can lift up or quell its roaring waves. In vapour how much variety is added to the view by the mist or the cloud, which by their ever-changing shadows diversify, at every moment, the landscape over which they are flitting; whilst the gorgeous hues of the clouds around the setting sun, and the glowing tints of the rainbow, are due to the refractive action of water and watery vapour upon the solar rays.

Properties.—At the ordinary temperature of the air, water, when free from admixture, is a clear, transparent liquid, destitute

of taste or smell, colourless when seen in a volume of small thickness, but exhibiting a pale blue tint when the light traverses a column of six feet, the colour passing to a deep bluish green as the depth of the water increases. At temperatures below 0° (32° F.) it freezes and assumes a variety of crystalline forms derived from the rhombohedron and six-sided prism. Water evaporates at all temperatures, and under the ordinary pressure of the atmosphere it boils at about 100° (212° F.). Its anomalous expansion by heat (143), and the important purposes thereby attained (151), as well as the great dilatation which it undergoes on freezing (76), have been already pointed out. Arago and Fresnel have shown, that notwithstanding the gradual dilatation of water at temperatures below 4° (39·2° F.), its refractive power on light continues to increase regularly, as though it contracted. Its density at 4° is taken as 1·000, and it forms the standard with which the specific gravities of all solids and liquids are compared. A litre of water, or cube of 10 centimetres in the side, at 4° weighs 1000 grammes, or 1 kilogramme; or in English weights and measures, a cubic inch of water at 62° F. weighs in air 252·456 grains, and a cubic foot very nearly 1000 (more exactly 997) ounces avoirdupois, the barometer standing at 30 inches.

To the chemist water is invaluable as a solvent. It is perfectly neutral to test papers, and enters into combination with various oxides forming the so-called acids and bases. Experience has shown that when an acid anhydride has once combined with water, the separation of the water from the compound is generally impracticable; if, however, some powerful base is presented to the acid, the water is again eliminated, and may be expelled by the application of heat. Suppose, for example, that sulphuric anhydride has been added to a large quantity of water; on heating the mixture the water passes off readily at first, leaving the less volatile acid behind, but by degrees it becomes necessary to increase the temperature in order to expel the water. At last the acid itself begins to evaporate, and then no further separation can be effected, because when the temperature rises to about 338° (640° F.) the entire liquid distils over. It is found on analysing the acid when it has reached this point, that the composition of the liquid may be represented very nearly by the formula H_2SO_4. But if to this concentrated acid, oxide of lead be added, water is eliminated, and anhydrous plumbic sulphate is obtained:

$$PbO + H_2SO_4 = OH_2 + PbSO_4.$$

$$[PbO + SO_2(OH)_2 = OH_2 + SO_2(O_2Pb)''.]$$

Upon the older view of the constitution of salts, which regards these bodies

as formed by the union of an anhydride with a base, the water would, in the foregoing instances, supply the place of a base, and it hence has been termed *basic* water, *e.g.*:—(if $H = 1$, $O = 8$, $S = 16$ and $Pb = 103$):

HO,SO_3, oil of vitriol: PbO,SO_3, sulphate of lead.

Still adopting the older view, it has been supposed in a similar manner that water combines with the powerful bases, such as potash or soda; it then cannot be expelled from them until some acid has been added. Potash in the form in which it is obtained by evaporating down its aqueous solution and heating the residue to dull redness, contains the elements of one equivalent of oxide of potassium and one of water, KO,HO: this equivalent of water cannot be expelled except by the addition of an acid, such as sulphuric acid; then, by the application of heat, anhydrous sulphate of potassa is obtained: $KO,HO + HO,SO_3 = 2HO + KO,SO_3$. In such a case the water in combination with the base appears to perform the part of an *acid*.

This older explanation is inadmissible if water be represented as consisting of OH_2; yet in the latter case the presence of hydrogen in potassic hydrate may be equally well accounted for, if it be supposed that caustic potash is a compound formed upon the same plan or type as water, but that it contains an atom of potassium in place of one of the atoms of hydrogen present in the molecule of water. Further, anhydrous potash, or potassic oxide (which may be formed from the hydrate of the alkali by heating it with potassium, hydrogen being liberated) is viewed as containing two atoms of potassium in place of the two atoms of hydrogen in the molecule of water. These relations of the three different compounds may be thus represented:

HHO	;	KHO	;	KKO.
Water.		Potassic hydrate.		Anhydrous potash.

The reaction of sulphuric acid upon potassic hydrate is then a true case of double decomposition, and may be thus represented:

$2KHO$	+	H_2SO_4	=	$2HHO$	+	K_2SO_4;
Potassic hydrate.		Sulphuric acid.		Water.		Potassic sulphate.
$[2OKH$	+	$SO_2(OH)_2$	=	$2OHH$	+	$SO_2(OK)_2]$

the two atoms of potassium of the base, and the two of hydrogen in the acid, changing places with each other, whilst potassic sulphate and water are simultaneously formed.

The compounds of water are frequently termed *hydrates*. When a body is described as being entirely free from water, it is commonly said to be *anhydrous* (from ἄ not, ὕδωρ water).

Many salts in crystallizing unite with a definite quantity of water, the amount of which, moreover, frequently varies, not only in different salts, but also with the same salt, the crystalline form of the salt depending on the number of molecules of water with which it is united. On the application of a gentle heat, this water

may be again expelled without altering the chemical properties of the saline body. In this case the water is spoken of as *water of crystallization.* For instance, borax always crystallizes with 10 molecules of water, $Na_2B_4O_7.10OH_2$, in oblique rectangular prisms, if the solution of the salt be not sufficiently concentrated to begin to crystallize until the temperature falls to 56° (133° F.); but from a more concentrated solution, borax is deposited in regular octohedra with only 5 molecules of water. So, again, sodic sulphate crystallizes, under ordinary circumstances, in oblique four-sided prisms with 10 molecules of water; but if a solution saturated at 33° (91° F.), be very slowly heated, the sulphate is deposited in rhombic octohedra which contain no water: crystals containing 7 molecules of water may also be obtained. Many salts part with their water of crystallization by mere exposure to air. Sodic carbonate, $Na_2CO_3.10OH_2$, for example, crumbles down or *effloresces* to a white powder; and the same thing occurs in the case of sodic sulphate $Na_2SO_4.10OH_2$. Other salts, on the contrary, absorb moisture from the atmosphere, and become damp or even liquefy in the water so absorbed; they are then said to *deliquesce.* Potassic carbonate, K_2CO_3, and calcic chloride, $CaCl_2$, offer instances of this kind.

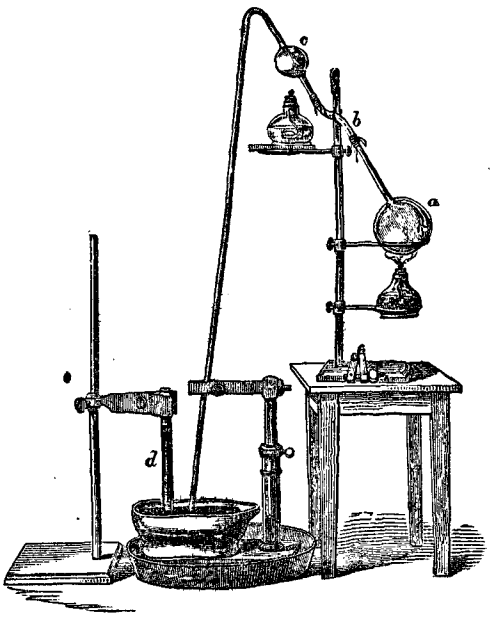
(350) **Natural Waters.**—Owing to its extensive solvent powers, water is never met with naturally in a state of purity.

Rain water, collected after a long continuance of wet weather, approaches nearest to it, but even that always contains atmospheric air to the extent of about $2\frac{1}{2}$ volumes of air in 100 of water, and also the other gases present in the air. The first fall of rain after an interval of dry weather always contains traces of nitrates and nitrites, and of ammonic salts, and often of common salt and some organic impurities. The ratio of nitrous to nitric acid in rain water depends to a great extent on the temperature, and also on the moisture and electricity of the atmosphere, calm cloudy weather, a moist atmosphere and moderate temperature favouring the production of nitrous acid, whilst a high temperature, dry winds, and thunderstorms increase the proportion of nitric acid.

The quantity of air which is contained in spring or other water can be readily ascertained in the following manner:—A globular flask, fig. 284, capable of containing 400 or 450 cub. centim., or from 14 to 16 ounces, such as is used for taking the density of vapours, is filled with the water to be examined, and connected by a vulcanized caoutchouc tube, *b*, to a piece of barometer tube, upon which is blown a bulb, *c*, 2 inches (5 cm.) or more in diameter. This tube is bent in the manner represented in the figure; the longer limb being upwards of 30 inches (760 $^{mm.}$) in length, and terminating below in a recurved extremity

designed to deliver the gas disengaged from the water, into a graduated jar, *d*, with an expanded funnel-shaped mouth, which is supported in a small mercurial bath. The bulb, *c*, having been about half-filled with the water, is connected with the flask by the caoutchouc tube, which is firmly secured at both ends by ligatures. A small wooden vice, such as is seen at *f*, is made use of to compress the vulcanized tube and to cut off communication between the flask and the bulb, *c*. The water in *c* is now made to boil briskly for ten minutes or a quarter of an hour, until all the air is expelled from the tube, the mouth of which is kept just below the surface of the mercury. When, after the boiling has been continued for a few minutes, no more air escapes from the tube, the jar, *d*, is filled with mercury and placed over the end of the long tube. The vice is removed, and heat applied to the flask, *a*; the water speedily begins to give off gas, and the quantity increases till the water boils. Gentle ebullition must be continued steadily for a full hour, and the operation terminated by a few minutes' brisk boiling, by which the delivery tube will be filled with steam, and all the air will be driven over into the jar. One object of the globe, *c*, is to prevent the water from boiling over into the jar, *d*: a little steam always condenses in the jar above the mercury, but this is a matter of small consequence. When the operation has terminated, the gas is allowed to cool, and is transferred to a tall jar of water or of mercury, where its bulk can be measured.

FIG. 284.



It will be found that all water, including even that which has been recently distilled, contains air. For example, three samples of water twice distilled in glass vessels, were submitted to experiment: 106 cub. centim. of the first specimen contained 1·85 c. c. of air; in the same bulk of the second 2·15, and the third specimen 2·38 c. c. of air were present; the oxygen and nitrogen being in each case almost exactly in the proportion of 1 measure of oxygen to 2 measures of nitrogen.

Spring Water, although it may be perfectly transparent, always contains more or less of saline matter dissolved in it. The nature of the salts will of course vary with the character of the soil through which the water percolates, but the most usual saline impurities are calcic carbonate and sulphate, common salt, and magnesic sulphate and carbonate. The waters of the New Red Sandstone are impregnated to a greater or less extent with calcic

sulphate; and the shallow wells in the gravel of the London district contain a considerable quantity of the same salt, to which they owe their hardness. Nitrates and ammonic salts are often abundant in these and other well-waters of towns, owing to contamination with sewage products, which have in many cases undergone partial oxidation. The nature and amount of the salts found in the waters of shallow wells vary considerably at different times, but the deep springs are very uniform when examined even at considerable intervals. Most spring waters are charged with a notable proportion of carbonic acid, which dissolves a considerable amount of calcic carbonate; the calcareous springs in the chalk districts around London contain from 255 to 285 mgrms. per litre, or from 18 to 20 grains of chalk per gallon, nearly one-third of which becomes separated by exposure of the water to the atmosphere, so that a running stream will seldom contain more than 11 or 14 grains of chalk per gallon in solution (170 or 200 mgrms. per litre). Waters which have filtered through a bed of chalk also frequently contain sodic carbonate in considerable quantity, as is the case with the deep-well waters of London.

Mineral Waters are waters impregnated with a large proportion of any one of the above-named salts, or with some substance not so commonly met with: such waters are usually reputed to possess medicinal qualities, which vary with the nature of the salt in solution. Many of these springs are of a temperature considerably higher than that of the surface of the earth where they make their appearance. At Carlsbad and Aix-la-Chapelle this temperature varies from 71° to 88° (160° to 190° F.). Such hot springs either occur in the vicinity of volcanoes, in which case they generally abound in carbonic acid, as well as in common salt and other salts of sodium, or they spring from great depths in the rocks of the earliest geological periods, and contain chlorides of calcium and magnesium, and almost always traces of sulphuretted hydrogen. (Berzelius.) The Geysers of Iceland are heated even beyond the temperature of 100° (212° F.) in the tube, and at intervals the boiling water is ejected with explosive violence. (See Tyndall, *Heat as a Mode of Motion*, 4th ed. 126.) The Geysers of the Yellowstone river no doubt owe their activity to the same cause.

Many mineral waters contain salts of iron in solution, which impart to them an inky taste; they are then frequently termed *chalybeate* waters; the Tunbridge Wells springs, and some of those at Cheltenham are of this kind. In other instances carbonic acid is very abundant, giving the brisk *effervescent* character

noticeable in Seltzer water, which also contains a notable proportion of hydric sodic carbonate ($NaHCO_3$, the so-called bicarbonate of soda), and the Vichy waters abound still more in this salt. Less frequently, as in some of the Harrogate and Moffat waters, sulphuretted hydrogen is the predominating ingredient, giving the nauseous taste and smell to such *sulphureous* waters. In other instances, the springs are merely *saline*, and contain purgative salts, like the springs at Epsom, which abound in magnesic sulphate, and at Cheltenham, where common salt and sodic sulphate are the predominant constituents. Many of these saline springs also contain small quantities of iodides and bromides, which add greatly to their therapeutic activity, whilst others contain organic matter, as is the case with those of the Barèges district in the Pyrénées. The Geysers are rich in silica, which in some cases forms nearly one-half of their soluble constituents.

River Water, although it often contains a smaller amount of salts, is less fitted for drinking than ordinary spring water, as it usually holds in solution a much larger proportion of organic matter of vegetable origin, derived from the extensive surface of country which has been drained by the stream. If the sewage of large towns situated on the banks be allowed to pass into the stream, it is of course still less fit for domestic use. Running water is, however, endowed with a self-purifying power of the highest importance, although it has recently been shown that this is not so great as was formerly supposed. (Report of Commission on the Pollution of Rivers, 1868. On the Mersey and Ribble Basins, 1870. Vol. i. p. 18). The continual exposure of fresh surfaces to the action of the atmosphere promotes the oxidation of the organic matter, and if the stream be unpolluted by the influx of the sewage of a large town, this process is generally fully adequate to preserve it in a wholesome state. River water almost always requires filtration through sand before it is fit for domestic use; and if waterworks designed to supply such water be properly constructed, provision is made for this filtration. Suspended matters, such as weeds, fish-spawn, leaves, and finely divided silt or mud, are thus removed; but vegetable colouring matter in solution, salts and other bodies dissolved in the water cannot, of course, be arrested by such a filter.

In the gradual percolation of water through the porous strata of the earth, many even of these soluble impurities are removed, particularly those of organic origin, partly by adhesion to the sur-

face of the filtering material, but chiefly by a slow oxidation in the pores of the soil.

The magnetic oxide of iron, indeed, seems to exert a peculiar influence in promoting the oxidation of organic matter contained in water which is allowed to percolate through it, and it appears probable that this action, to which Mr. Spencer has particularly called attention, may furnish a valuable auxiliary to the methods of filtration at present in use. Filtration through beds of iron turnings has likewise been practised in some cases with similar advantages, but the oxygen is in this case in great measure absorbed from the water by the iron: Mr. G. Bischof has adopted a modification of this principle in the construction of his spongy iron filter, in which the water passes first through a layer of spongy iron about 8 inches thick, and then through 4 inches of powdered marble or limestone to remove the iron dissolved by the water as ferrous carbonate. This filter removes a large proportion of the dissolved putrescible organic matter from water; in all probability the ferric oxide which is formed acts as a carrier of oxygen, being reduced to ferrous oxide by the organic matter which it oxidizes, whilst the the ferrous oxide is again oxidized to ferric oxide by the oxygen dissolved in the water. Animal charcoal also exerts a marked effect in promoting the oxidation of organic matters in solution, and constitutes an excellent filtering material.

The presence of organic matter in water is easily ascertained by the reducing influence which it exerts upon chloride of silver or of gold, when boiled with them. The argentic chloride becomes purplish, and auric chloride imparts a brown tint to the water under such circumstances, owing to the precipitation of metallic gold. Even at ordinary temperatures, a very dilute acidulated solution of potassic permanganate is rendered nearly colourless, by reduction to a lower state of oxidation. This test, although easily applied, is not a certain indication of the presence of organic matter: thus the presence of mineral reducing agents, such as ferrous salts and nitrites, will cause the decoloration of a solution of the permanganate, and on the other hand there are many organic bodies which reduce potassic permanganate so slowly that their presence might be entirely overlooked. This is the case with urea, sugar, creatin, and hippuric acid. Oxalic acid appears to be the only organic body which reduces the permanganate completely in the cold within 10 minutes.

Water is familiarly spoken of as *hard* or *soft*, according to its

action on soap. Those waters which contain compounds of calcium or magnesium occasion a *curdling* of the soap, as these bodies produce with the fatty acid of the soap a substance not soluble in water. Soft waters do not contain these salts, and dissolve the soap without difficulty. Many hard waters become softer by boiling, the carbonic acid being expelled by this means, and the calcic carbonate and part of the calcic sulphate which were held in solution are then deposited, and cause a 'fur' or incrustation upon the inside of the boiler. Such waters admit of being softened considerably by the addition of a certain proportion of lime water. The excess of carbonic acid which keeps the calcic carbonate in solution, being removed by the lime of the lime water, so that both the lime present in the water as carbonate and that in the lime water itself are thrown down as calcic carbonate. This process, which is known as Clark's process, is now successfully applied on a large scale to waters containing much calcic carbonate in solution. When the hardness is owing to calcic or magnesic sulphates, the addition of sodic carbonate precipitates the carbonates of these metals and softens the water, as is practically known to laundresses.

Sea Water is largely impregnated with common salt and magnesic chloride, to which it owes its saline, bitter taste. It might be supposed that the quantity of salts which it contains is continually on the increase, as the sea is the receptacle for all the fixed contents of the water which is discharged into the ocean by rivers, pure water alone evaporating from the surface of the former; there is, however, a return to the surface of the soil provided for in the marine plants, and fish, which are perpetually being raised from its depths by the force of storms, by predatory birds, and by the industry of man. The specific gravity of sea water is subject to trifling variations, according to the part of the globe where it is collected. The waters of the Baltic and of the Black Sea are less salt than the average, whilst those of the Mediterranean are more so. The waters of the Mediterranean in the Levant are more salt than those of the same sea near the Straits of Gibraltar. The mean specific gravity of sea water is 1·027, and the quantity of salts ranges from 3·5 to 4 per cent. An analysis of the water of the British Channel, according to Schweitzer (*Phil. Mag.* 1839, xv. 58) is given below, as also one of the Irish Sea by Thorpe and Morton (*Jour. Chem. Soc.* 1871, xxiv. 506) together with that of the Mediterranean, analysed by Usiglio (*Ann. Chim. Phys.* 1849 [3], xxvii. 104); they will be seen to agree very closely in composition:

	British Channel.	Irish Sea.	Mediterranean.
Water	963·74372	966·14054	962·345
Sodic chloride ...	28·05948	26·43918	29·424
Potassic chloride ...	0·76552	0·74619	0·505
Magnesic chloride ...	3·66658	3·15083	3·219
Magnesic bromide ...	0·02929	0·07052	0·556
Magnesic sulphate ...	2·29578	2·06608	2·477
Calcic sulphate ...	1·40662	1·33158	1·357
Calcic carbonate ...	0·03301	0·04754	0·114
Iodine	traces		
Ammonic chloride ...	traces	0·00044	
Ferrous carbonate ...		0·00503	0·003
Magnesic nitrate ...		0·00207	
	1000·00000	1000·00000	1000·000
Specific gravity ...	1027·4 at 16°	1024·84 at 15°	1025·8 at 21°

An elaborate paper on the composition of sea water in various parts of the world, by G. Forchhammer, will be found in the *Phil. Trans.* for 1865, p. 203. Minute quantities of fluorine, manganese, barium, strontium, and aluminium, as well of silica, boracic acid, and phosphates, have been found in the waters of the ocean, but nitrates have as yet eluded the most careful observation. Silver, lead, copper, and arsenic have been detected either in sea water itself, in the ashes of marine plants and animals, or in the deposit formed in steam boilers fed with sea water.

(351) **Distilled Water.**—For chemical purposes, water is always purified by distillation, which may be effected on a small scale in glass retorts, and more conveniently on a large scale in a copper still provided with a tin or copper worm. Iron pipes may also be safely used for the purpose of condensation, but lead must be avoided, and the still should not be employed for any other purpose. The addition of lime to the water before submitting it to distillation is useful, as it retains the excess of carbonic acid, and also traces of hydrochloric acid, which are apt to pass over if magnesic chloride be present, owing to the decomposition of this salt. The first portions of water should be rejected, because they usually contain traces of ammonia; pure distilled water, if free from ammonia will give no colouration on the addition of Nessler's test (681). As, however, distilled water is apt to contain volatile nitrogenous carbon compounds, it is necessary, when it is required chemically pure, to distil it first with a little potassic hydrate and permanganate, and then with a little hydric potassic sulphate to retain the last traces of ammonia. When a few drops of distilled water are evaporated upon a slip of glass, no stain or mark should be left, otherwise some saline impurity is present.

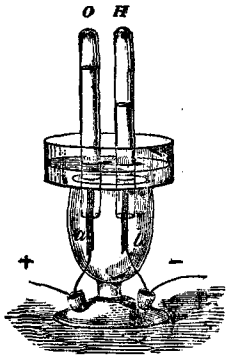
Distilled water is now largely prepared on long sea voyages, the ships of H.M. navy being fitted with suitable distillatory apparatus. As organic matter is present both in ordinary water and in sea water, the distillate is liable to acquire a disagreeable taste in consequence of a portion of the impurities undergoing decomposition during distillation. This, however, is entirely got rid of by filtration through charcoal, after due aëration, which renders the water agreeable and wholesome as a beverage.

Composition of Water.—Water was long supposed to be an elementary substance; this, as we have seen, is not the case, it being a compound of hydrogen with oxygen in the proportion of two atoms of the former to one of the latter. Its formula is therefore OH_2 [or OH_2], and its molecular weight 18. When converted into vapour, 18 grammes of steam occupy twice the bulk of 1 gram of hydrogen at the same temperature; the molecular volume of aqueous vapour is therefore [□], if the atomic volume of hydrogen be taken as □. Its composition is shown in the following table:

	Symb.		By weight.	Dumas.	By vol.
Oxygen	O	=	16 or 88·89	88·88	1
Hydrogen	H_2	=	2 or 11·11	11·12	2
	OH_2		18 100.00	100.00	2

An elegant mode of showing the composition of water analytically is afforded by the voltaic battery. A glass vessel, Fig. 285, containing two platinum plates, *a* and *b*, is filled with water, slightly acidulated with sulphuric acid to improve its conducting power, and is arranged so that the current of a battery consisting of three or four of Grove's cells may be passed through it (266). Immediately the two platinum plates are connected with the wires of the battery, bubbles of gas form on the plates; and if two similar jars be filled with water, and one inverted over each plate, the volume of the gas which rises from the platinode or negative plate *b*, will be found to be exactly double of that which rises from the zincode or positive plate, *a*. The gas in the tube O is oxygen, and rekindles a glowing match, whilst that in H is hydrogen, extinguishing flame, but taking fire when a light approaches it.

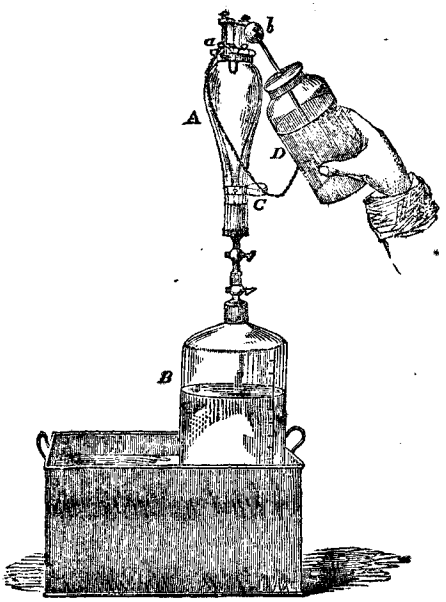
FIG. 285.



(352) **Synthesis of Water—Eudiometers.**—If a cold glass bell jar be held over a burning jet of dry hydrogen, the interior quickly becomes bedewed with moisture, owing to the formation of water by the union of the hydrogen with the oxygen of the atmosphere. A mixture of oxygen and hydrogen may be kept at the ordinary temperature for an unlimited period without entering into combination; but the passage of an electric spark, the application of a lighted or even of a glowing match, and, in some instances, the mere contact of a cold metallic substance, such as platinum, especially if the metal be in a finely divided state (65), is sufficient to determine their immediate combination. The heat evolved on the sudden compression of the mixed gases, produces the same effect, whilst a much greater amount of compression fails to cause their union, if it be applied gradually, even if raised until it is equal to that of 150 atmospheres.

Cavendish, in his investigations on the formation of water, effected the combination of the two gases by means of the electric spark. For this purpose he employed a strong glass vessel, a modification of which is represented at A, fig. 286. Through the upper part, two platinum wires are inserted to within $3^{mm.}$, or the eighth of an inch of each other. The vessel can be closed at the bottom by a glass stopcock, *c*. The air is exhausted, and the vessel screwed upon the top of a jar, B, containing a mixture of two measures of hydrogen and one of oxygen; on opening the stopcocks a portion of the mixture enters the vessel; the cocks are then closed, and an electric spark passed through the mixture, by discharging a small Leyden jar, D, through the platinum wires, *a*, *b*.* A bright flash is seen at the moment of the discharge, and the gases unite to form aqueous vapour, which becomes condensed on the sides of the glass: the whole of the two gases, if mixed in the above proportions, enter into combination with each other. On again opening the stopcocks, a fresh quantity of the mixed gases may be admitted, to supply

FIG. 286.



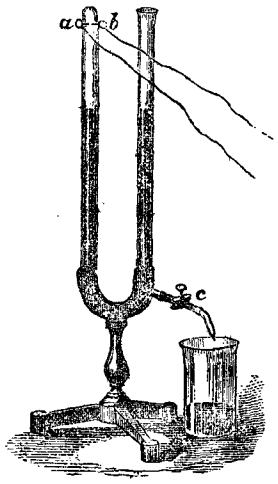
* In all such cases, the discharge from the secondary current of an induction coil may be advantageously substituted for the spark of the Leyden jar.

the place of those just combined, the spark again passed, and the process repeated until the whole of the gases are consumed, and an appreciable quantity of water formed.

The uniformity in the composition of chemical compounds, and the constant proportion in which the elements combine with one another, are strikingly illustrated by means of a mixture of oxygen and hydrogen gases. The two gases may be mixed in any arbitrary proportion in a suitable vessel, into the sides of which two platinum wires are fused for the purpose of transmitting the electric spark. If the mixture be capable of exploding at all, combination will be found to have occurred in the proportion of two measures of hydrogen to one measure of oxygen, no matter in what proportion the gases were originally mixed. If oxygen be used in excess, the superfluous oxygen will be found remaining uncombined; and if hydrogen be in excess, the excess of hydrogen will be left unaltered after the transmission of the spark.

A valuable instrument, called the *Eudiometer*, is constructed upon this principle, by means of which various gaseous mixtures may be analyzed with great exactness. Of the many different forms of this instrument which are in use, one of the most convenient is that devised by Hofmann. It consists of a stout syphon tube, fig. 287, open at one extremity and closed at the other. Into the sides of the tube, near the sealed end, two platinum wires, *a*, *b*, are fused, for the purpose of transmitting an electric spark across the tube, the sealed limb being accurately graduated to tenths of a cubic centimetre, or other suitable divisions. Suppose it be desired to ascertain the proportion of oxygen in atmospheric air; a small quantity of air is introduced into the instrument, which has been previously filled with mercury, and the bulk of this air is then accurately measured, taking care that the level is the same in both tubes, which is easily effected by adding more mercury, or by drawing it off through the caoutchouc tube fixed upon the small outlet tube just above the bend, and which is closed by means of a screw tap, *c*. A quantity of pure hydrogen about equal in bulk to the air is next introduced, and the volume of the mixture again accurately measured. The open extremity of the tube is now closed with a tightly-fitting cork, leaving a column of atmospheric air between it and the mercury; this portion of air acts as a spring when the mixture in the closed limb of the eudiometer is exploded by the passage of the electric spark. The remaining gas now occupies a smaller volume, owing to the condensation of the steam which has been formed by the union of the oxygen contained in the atmospheric air with a portion of the hydrogen, so that mercury must be poured into the open limb until it stands at the same level in both tubes, before the volume of the gas is measured for

FIG. 287.

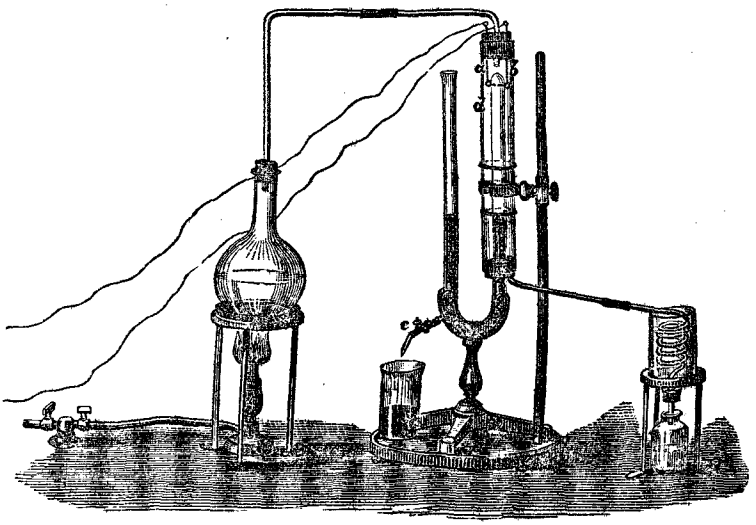


the third time. One-third of the reduction in bulk experienced by the gas will represent the entire volume of oxygen which the mixture contained. For accurate experiments Regnault has contrived a very complete, though costly, form of eudiometer upon this principle. (*Ann. Chim. Phys.*, 1841 [3], xxvi. 333.)

A modification of the foregoing experiment enables us to show that the volume of aqueous vapour which is formed by the union of oxygen with hydrogen occupies a space exactly equal to two-thirds of that of its constituent gases, or that 2 volumes of hydrogen and 1 volume of oxygen furnish by their union 2 volumes of steam.

For this purpose the closed limb of the syphon eudiometer is surrounded by a second wider tube, as shown at *d*, fig. 288, provided with an exit tube and

FIG. 288.



condenser below. A mixture of 2 volumes of hydrogen and 1 of oxygen—such as is furnished by the electrolytic decomposition of water—is introduced into the sealed limb, of which it should occupy 5 or 6 inches (12 or 15$^{cm.}$). A gentle current of vapour from a small flask, containing fousel oil which boils at 132° (269°·6 F.), is then passed for some minutes through the wide tube, so as to bring the mixed gases to the temperature of 132° (269°·6 F.) The mercury in the two limbs is made level, and the height at which the expanded gas stands is then marked by means of an elastic band which slides on the outer tube. The eudiometer is now closed with a cork, and the electric spark passed, whilst the current of vapour is still maintained; the gases combine with a flash, and the volume of the vapour produced is seen to be less than that of its constituent gases. If now the mercury in the two limbs of the eudiometer is again levelled, it will be seen that the aqueous vapour occupies a volume exactly two-thirds of that of the gases originally employed.

If a mixture of oxygen and hydrogen be fired in the air in considerable quantity, as when a bladder-full is ignited,—or, what is still better, when a quantity of soapsuds is blown up into bubbles by forcing some of the gaseous mixture out of a

bladder through the extremity of a tube dipping into the liquid —a loud and sharp report is produced; the steam which is formed expands suddenly from the high temperature attendant on the combustion, and immediately afterwards becomes condensed: great dilatation first occurs, followed by the formation of a partial vacuum, thus producing an assemblage of sound waves that cause the sensation of a loud report. If the hydrogen be mixed with air, a similar but feebler explosion occurs when a light is applied; hence it is especially necessary in all experiments with hydrogen to allow time for the expulsion of the atmospheric air from the apparatus before setting fire to the issuing gas. The explosion is most violent when 2 measures of hydrogen are mixed with 5 of air: if the mixture be diluted with a large excess either of hydrogen or of air, the explosion becomes more feeble, the heat evolved is less intense, and the combustion less sudden, until at a certain degree of dilution no explosion occurs, the mixture merely burning slowly; if still further diluted, it takes fire only just at the spot where the heat is applied, but the combustion does not spread through the mass.

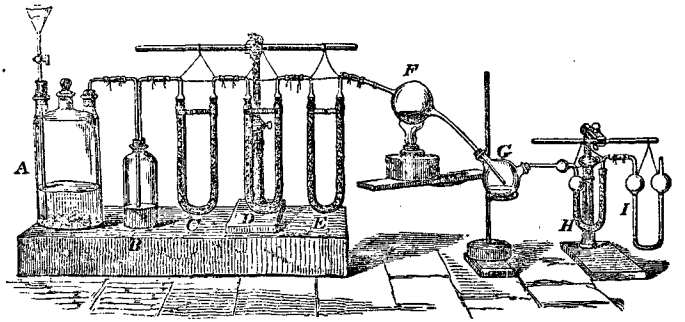
If a tube about two feet long and open at both ends, be placed over a jet of burning hydrogen, the flame will suddenly elongate itself, and at the same time a clear musical note will be heard; this is caused by a series of small explosions that succeed each other so rapidly and at such regular intervals as to give rise to a musical sound, the pitch and quality of which varies with the size of the flame and with the length and diameter of the tube.*

Pure water may be formed in considerable quantities by a method differing from those hitherto described, the operation at the same time furnishing a means of ascertaining accurately the relative weights of oxygen and hydrogen which enter into the composition of water. At a red heat, hydrogen deprives cupric oxide of its oxygen, uniting with the latter to form water, so that by passing a current of hydrogen over a weighed quantity of the oxide, and determining the weight of the water thus produced, and the loss sustained by the oxide, the proportion of hydrogen which has combined with the oxygen can be calculated. The apparatus required for this purpose is represented in fig. 289. A quantity of cupric oxide is placed in the globe, F, which is constructed of refractory glass, and the globe and its contents are then accurately weighed. A current of hydrogen, prepared from zinc and sulphuric acid in the bottle, A, is allowed to bubble up through a solution of potassic hydrate, B, and to traverse three bent tubes in succession; the first, C, is filled with fragments of pumice-stone moistened with a solution of corrosive sublimate, $HgCl_2$, the second, D,

* For a detailed account of these singing flames we must refer the reader to an article by Prof. Tyndall published in the *Philosophical Magazine* for July, 1857.

contains fragments of fused potassic hydrate, and the third, E, is charged with pumice moistened with oil of vitriol. The mercuric salt and the potash remove the traces of arsenicum, sulphur, and carburetted compounds, which the gas might otherwise carry over, and the oil of vitriol absorbs the last traces of moisture, so that the hydrogen when it arrives at F is dry and pure. As soon as the air is completely displaced, heat is applied to the globe; the cupric oxide is then decomposed, its oxygen uniting with the hydrogen to form water, whilst metallic copper is left. The water is mostly condensed in the receiver, G; the small

FIG. 289.



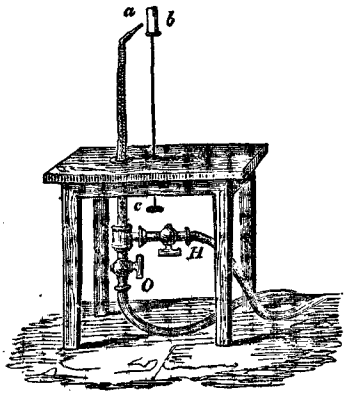
amount of vapour which passes off, being completely absorbed in the bent tube, H, filled with fragments of pumice moistened with oil of vitriol: the whole of the water is by this means arrested. I is a bulb tube containing a little oil of vitriol, which prevents the entrance of extraneous moisture, and also serves to show when the operation is terminated by the passage of free hydrogen through the acid. When the globe, F, is cold, the hydrogen is displaced by a current of air, and on weighing it at the termination of the experiment, the loss gives the quantity of oxygen which has combined with the hydrogen, whilst the difference between the amount of oxygen and that of the water condensed in the receiver, G, and the drying tube, H, shows the quantity of hydrogen that has combined with it. Two grams of hydrogen are in this manner proved to require exactly 16 grams of oxygen for their conversion into water. (Dumas, *Ann. Chim. Phys.*, 1843, [3], viii. 189.)

Many other metallic oxides besides oxide of copper, when heated in a current of hydrogen, part with their oxygen, and are reduced to the metallic state. If the bulb be weighed first when empty, then when charged with oxide, and a third time after the stream of gas has been continued until the formation of water ceases, and the tube has become cold, the loss of weight sustained by the oxide furnishes the proportion of oxygen combined with the metal. A true and very accurate analysis of the oxide will thus have been effected: 79·4 parts of cupric oxide are found in this way to contain 63·4 of copper and 16 of oxygen.

(353) **Oxy-hydrogen flame.**—Hydrogen in the act of combining with oxygen gives a most intense heat. By passing a jet of oxygen into a flame of coal-gas or hydrogen, or still better b introducing a jet of oxygen, as at O, fig. 290, into the centre of a jet connected at H with a gas-holder supplying

hydrogen, so that the two gases may become mixed just before they issue from the common orifice of the tube, *a*, a heat may be obtained which can scarcely be surpassed by chemical means. Sometimes the two gases are mixed in the proportion of 2 volumes of hydrogen to 1 volume of oxygen, and burned through a tube of particular construction, known as Hemming's safety jet. It consists of a brass tube, about 6 inches or 15 centimetres long, and two-thirds of an inch ($16^{mm.}$) in diameter, filled with pieces of very fine brass wire, which are packed closely together, and then wedged in very tightly by driving a stout conical piece of wire into the axis of the tube. This tube has a blowpipe jet at one extremity, and at the other a screw which can be connected with a stopcock adjusted to the neck of a bladder containing the mixed gases. The temperature produced by their combustion is so intense that thick platinum wire is melted with ease, and partially volatilized: iron and steel burn with vivid scintillations. Rock crystal also may be liquefied, and drawn out into threads like glass, and the stem of a tobacco pipe may be fused into an enamel-like bead. When the oxy-hydrogen flame, which is but very feebly luminous, is directed upon a small cylinder of lime, *b*, the lime does not fuse, but becomes intensely heated, emitting a very pure white light of great steadiness and brilliancy. This may be maintained for hours, if care be taken to expose to the flame fresh surfaces of the lime by causing the cylinder to revolve slowly, by means of clockwork, or less perfectly, by occasionally turning the pin, *c*, which supports the lime. Without this precaution, a cavity would be formed opposite to the jet, from volatilization or mechanical abrasion of a small quantity of the lime. This light was originally proposed by Lieut. Drummond, to be used in the trigonometrical survey of Great Britain, and when the rays are concentrated by a parabolic reflector it may be seen at very great distances. On the 31st December, 1845, it was seen across the Irish Channel at half-past 3 P.M. (during daylight) from the top of Slieve Donard, in Ireland, by an observer stationed at the top of Snowdon,—an interval of 108 miles in a direct line; and it has more than once been seen at a distance of 112 miles.

FIG. 290.



Water is formed abundantly whenever combustible bodies which contain hydrogen are burned with free access of air. Wood, tallow, oil, wax, alcohol, coal-gas, and most of our ordinary combustibles which burn with flame, furnish considerable quantities of water in this manner.

A striking experiment may be performed with hydrogen, which shows how purely conventional are the terms 'combustible,' and 'supporter of combustion.' Let a tall bottle with a narrow neck be filled with hydrogen gas; through a cork which passes easily into the neck of the bottle fit a jet connected with a gas-holder containing oxygen; hold the bottle mouth down-

wards and set fire to the hydrogen, then immediately insert the cork and jet, through which a stream of oxygen is gently issuing. The flame will appear to attach itself to the tube conveying the oxygen, and the jet of oxygen will be burning in an atmosphere of hydrogen. Combustion, in fact, occurs at the place where the two gases come into contact. Suppose, for a moment, that the earth's atmosphere had contained hydrogen instead of oxygen; oxygen would have appeared to us in the light of a combustible gas, and hydrogen in that of a supporter of combustion.

(354) **PEROXIDE OF HYDROGEN**; *Hydric dioxide*, or *Hydroxyl* ($O_2H_2 = 34$) $\left[\begin{matrix}OH\\OH\end{matrix}\right]$; *Density of Liquid*, 1·453. Water is not the only compound of oxygen with hydrogen. Thénard in the year 1818, discovered a remarkable substance, which as it contains 2 atoms of oxygen in combination with 2 atoms of hydrogen, is termed *peroxide of hydrogen.*

Preparation.—In consequence of the unstable character of hydric peroxide, it is somewhat difficult to obtain it in a pure state. To procure it, an indirect process is adopted, which, though simple enough in principle, is somewhat tedious and complicated:—Caustic baryta, BaO, when heated to dull redness in a current of oxygen, combines with an additional atom of the latter, and becomes baric dioxide, BaO_2, which unites readily with water forming a hydrate, $BaO_2.6OH_2$. Hydric peroxide is obtained from this hydrated compound by decomposing it with hydrochloric acid.

The hydrated baric dioxide, reduced to a paste by grinding it in a mortar with water, is added in small quantities at a time to hydrochloric acid diluted with water, and kept cool by immersing the vessel in ice and water; the dioxide is gradually dissolved without effervescence, baric chloride and peroxide of hydrogen being formed:

$$BaO_2.6OH_2 + 2HCl = O_2H_2 + 6OH_2 + BaCl_2.$$

$$\left[\begin{matrix}O\\O\end{matrix}\right\}Ba'',6OH_2 + 2HCl = \left\{\begin{matrix}OH\\OH\end{matrix}\right. + 6OH_2 + BaCl_2\Big]$$

When the hydrochloric acid is nearly saturated with the dioxide, the baric chloride is decomposed by the cautious addition of dilute sulphuric acid; an insoluble baric sulphate is thus precipitated, whilst the liberated hydrochloric acid is able to decompose a fresh quantity of baric dioxide, which must be added with the same precautions as at first. The addition of sulphuric acid produces no change on the hydric peroxide which is present in the solution: it is merely an expedient for getting rid of the barium and setting free the hydrochloric acid.

After the removal of the baric sulphate by filtration, the liquid obtained is simply a very dilute solution of hydric peroxide with an excess of hydrochloric acid. This acid is again able to decompose a fresh portion of the baric dioxide.

The same series of operations is repeated upon the liquid three or four times in succession, alternately adding baric dioxide, and removing the barium in the form of baric sulphate, until a liquid is obtained which consists of dilute hydric peroxide containing 30 or 40 times its bulk of oxygen, and a large quantity of hydrochloric acid. The hydrochloric acid has now to be removed, and this is effected by adding argentic sulphate, until a trace only of hydrochloric acid is left in the liquid.* Sulphuric acid is thus substituted for the hydrochloric acid, which is precipitated in the form of the insoluble argentic chloride, whilst the hydric peroxide remains unchanged in the liquid. The sulphuric acid is now removed as baric sulphate by the careful addition of baryta water, which is at last added drop by drop, so as to avoid introducing any excess of baryta: the liquid is once more filtered, and is now a solution of hydric peroxide in water. In order to obtain the hydrate peroxide, the liquid is transferred to a basin and placed over sulphuric acid in the exhausted receiver of the air-pump; the water then evaporates much more rapidly than the peroxide, leaving the latter in a concentrated form. Dilute solutions of the peroxide may also be concentrated to a considerable extent by exposing them to a low temperature and removing the ice which is formed.

Pelouze substitutes silicofluoric acid for hydrochloric acid in decomposing the baric dioxide; it shortens the operation by removing the barium at once in the form of an insoluble baric silicofluoride. Baric dioxide may also be decomposed by suspending it in water, through which a current of carbonic anhydride is passed, but the solution so obtained is dilute.

The most convenient process for the preparation of the peroxide, however, is that proposed by Thomsen (*Deut. chem. Ges. Ber.*, 1874, vii. 73), who adds pure moist hydrated baric peroxide to sulphuric acid, diluted with about 5 or 6 times its weight of water, until it is nearly neutralized, keeping the mixture cool: then allows the baric sulphate to subside and filters. The trace of sulphuric acid, still in solution, may be exactly precipitated by the cautious addition of baric hydrate, and the solution of hydric peroxide concentrated in the usual way.

Schönbein has shown (*Ann. Chim. Phys.*, 1860 [3] lviii. 479) that in various processes where ozone is formed, small quantities of hydric peroxide are also produced; and in the electrolysis of acidulated and saline solutions when ozone is formed, traces of the peroxide are likewise produced if the operation is conducted at a low temperature, the proportion of gaseous oxygen collected in the voltameter being then always a little below the theoretical quantity. Hydrogen peroxide is also produced in small quantity during the combustion of a mixture of oxygen and hydrogen, and from Schöne's experiments (*Deut. chem. Ges. Ber.*, 1874, vii. 1693), would appear to be present in the air in minute quantity.

Properties.— In its most concentrated state, hydric peroxide is a colourless liquid, of syrupy consistence, with an odour somewhat resembling that of chlorine very much diluted; it remains liquid at a temperature of —30° (—22° F.). This peroxide is a very unstable compound; a temperature of about 20° (68° F.) is sufficient to cause the oxygen to begin to escape in small bubbles, and when heated to the boiling-point of water, the gas is evolved with a rapidity almost amounting to an explosion. The liquid is miscible with water in all proportions, and when diluted is less

* Oxide of silver cannot be substituted for the sulphate, as it would immediately cause the decomposition of the hydric peroxide.

easily destroyed by elevation of temperature, although even then ebullition for a few minutes is sufficient to expel the whole of the additional atom of oxygen, water alone remaining. This circumstance furnishes an easy method of analysing hydric peroxide. A given weight of the liquid is placed in a small retort, and diluted with 10 or 12 times its bulk of water; the temperature is raised to ebullition, oxygen is given off freely, and the gas is collected over mercury and measured when cold: the weight of the oxygen can be calculated from its bulk, and deducting the weight thus obtained from that of the peroxide operated upon, it will be found that for each 16 mgrms. of oxygen expelled, a little more than 18 of water remain; consequently allowing for the presence of a minute quantity of water contained in the peroxide, as water contains 2 mgrms. of hydrogen combined with 16 of oxygen, hydric peroxide will contain 2 mgrms. of hydrogen united with 32 of oxygen. Hydrogen peroxide is also readily soluble in ether, so that if an aqueous solution of the peroxide be agitated with the latter, it dissolves: this ethereal solution is much more stable than the aqueous one, and may be distilled without decomposition.

Hydric dioxide bleaches a solution of litmus, and many other vegetable colours: a drop of it, if placed upon the tongue blanches it, and destroys sensation for a time, the taste of the liquid being astringent and somewhat metallic. By means of hydric peroxide, the black plumbic sulphide, PbS, is converted into the white sulphate of the metal, $PbSO_4$, and many metallic protoxides become oxidized to peroxides. It also possesses the power of liberating iodine from potassic iodide in solution; and that even in the presence of ferrous sulphate. In this way, if starch paste be added to the solution, a most delicate test for the peroxide is obtained, 1 part in twenty million of water giving a distinct blue tinge.

One of the most remarkable properties of hydric peroxide, however, is that not only is it decomposed by substances which possess an attraction for oxygen, but the mere contact of many finely divided metals and metallic oxides which do not themselves undergo any change, occasions its decomposition; gold, silver, and platinum produce an instantaneous evolution of oxygen gas, which is the more rapid, the finer the subdivision of the body by which the decomposition is occasioned. A similar effect is produced by contact with the oxides of these metals, or with peroxide of manganese or lead. It is especially noteworthy that the oxides of silver, gold, and platinum not only decompose per-

oxide of hydrogen, but they are themselves reduced to the metallic state. These decompositions are all rendered less rapid by the addition of a few drops of sulphuric or hydrochloric acid, and are hastened by the presence of an alkaline hydrate. If hydric peroxide in its concentrated form be allowed to fall drop by drop upon argentic oxide, or black oxide of manganese, or upon finely divided metallic silver, platinum, or osmium, it is decomposed with explosion and great elevation of temperature.

CHAPTER VI.

OXIDES AND OXACIDS OF CHLORINE.

(355) THE attraction of chlorine for oxygen is so feeble that the two elements do not enter directly into combination with each other. Several compounds of oxygen and chlorine may, however, be obtained by indirect methods, three of which have been isolated; they are the following:

			Mol. vol.	In 100 parts. Cl.	O.
Hypochlorous anhydride ...	Cl_2O	= 87	⬚	81·60	+ 18·40
Chlorous anhydride ...	Cl_2O_3	= 119	⬚	59·66	+ 40·34
Chloric peroxide, or dioxide	ClO_2	= 67·5	⬚	52·59	+ 47·41
or	Cl_2O_4	= 135	⬚		

Four monobasic oxidized acids of chlorine may also be obtained, viz.:

Hypochlorous acid	$HClO$	= 52·5
Chlorous acid	$HClO_2$	= 68·5
Chloric acid	$HClO_3$	= 84·5
Perchloric acid	$HClO_4$	= 100·5

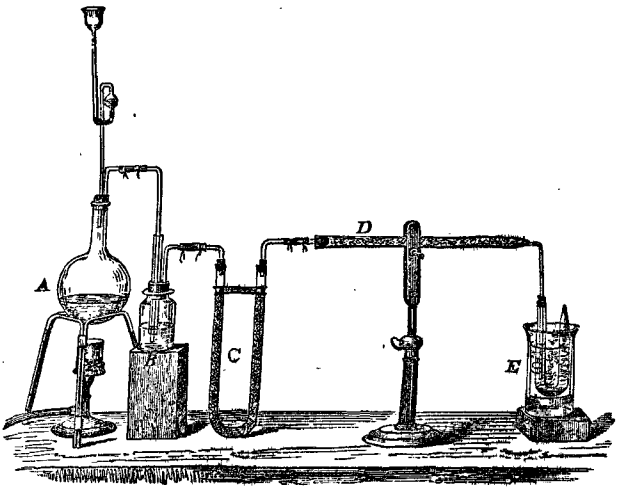
Millon's experiments have rendered it probable that other oxidized compounds also exist, the result of the combination of some of those already mentioned with the chloric and perchloric anhydrides.

(356) **HYPOCHLOROUS ANHYDRIDE**, $Cl_2O=87$ or $[OCl_2]$; *Mol. Vol.* ⬚; *Rel. wt.* 43·5; *Theoretic Density* 3·01; *Boiling-pt.* about 20° (68° F.).—If dry chlorine be passed slowly through a tube, D, fig. 291, filled with well-dried mercuric oxide, obtained by precipitating a solution of corrosive sublimate with potassic hydrate, an action takes place and a gas is produced which may be liquefied by surrounding the tube receiver, E, with a mixture of ice and salt. The chlorine is prepared in the flask, A, washed with water in the bottle, B, and dried by allowing it to

traverse the bent tube, c, filled with fragments of pumice-stone moistened with concentrated sulphuric acid.

The reaction between the chlorine and mercuric oxide appears to be very simple: 2 atoms of chlorine displace 1 atom of oxygen in the mercuric oxide, and this oxygen at the moment of its liberation unites with two other atoms of chlorine to form hypochlorous anhydride; $HgO + 2Cl_2 = HgCl_2 + Cl_2O$. The mercuric chloride, however, unites with a portion of the unattacked oxide producing a brown crystalline oxychloride. Hypochlorous anhy-

FIG. 291.



dride as thus prepared is a dark red liquid, which boils at 20° (68° F.). It emits a vapour of a deeper colour than that of chlorine, and having a peculiar suffocating chlorous smell. This vapour is remarkable for the ease with which it is decomposed into chlorine and oxygen; contact with sulphur, selenium, or phosphorus, the passage of an electric spark, or even the warmth of the hand or the vibration caused by making a scratch with a file on the glass tube containing it being sufficient to cause it to explode. On this account, it is necessary during its preparation to guard against any rise of temperature in the tube containing the mercuric oxide: 2 volumes of the anhydride in this way produce a mixture of 2 volumes of chlorine and 1 volume of oxygen. The composition of the gas is therefore as follows:

		By weight.	By volume.
Chlorine	Cl_2 =	71 or 81·6	... 2
Oxygen	O =	16 18·4	... 1
Hypochlorous anhydride ...	Cl_2O =	87 100·0	... 2

(357) **HYPOCHLOROUS ACID**; *Hydric hypochlorite*; $HClO = 52{\cdot}5$ [OClH or Cl(OH)].—Water dissolves about 200 times its bulk of gaseous hypochlorous anhydride, forming a pale yellow solution, which has an acrid, but not sour taste; $Cl_2O + OH_2 = 2HClO$; $[OCl_2 + OH_2 = 2OClH]$.

1.—When chlorine acts upon the oxides of metals which have but a feeble attraction for oxygen, these bases are often completely decomposed. Advantage was taken of this reaction in the preparation of hypochlorous anhydride, and a weak solution of hypochlorous acid may easily be obtained by agitating 1 part of red mercuric oxide with 12 of water in a large bottle of chlorine gas, care being taken that the mercuric oxide is in slight excess. The chlorine is rapidly absorbed; part of the oxide of mercury is decomposed by the chlorine, and the mercuric chloride thus produced unites with the unchanged mercuric oxide, forming a brown insoluble oxychloride of that metal; the solution on being decanted is found to contain hypochlorous acid; a more concentrated solution may easily be obtained by treating chlorine hydrate (p. 26) with precipitated mercuric oxide in slight excess. The reaction is as follows:

$$\underset{\text{Water.}}{OH_2} + \underset{\text{Mercuric oxide.}}{3HgO} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Oxychloride of mercury.}}{2HgO.HgCl_2} + \underset{\text{Hypochlor. acid.}}{2HClO.}$$

$$OH_2 + 3HgO + 2Cl_2 = \begin{matrix} HgCl \\ O \\ Hg \\ O \\ HgCl \end{matrix} + 2Cl(HO)$$

2.—A very interesting method of forming hypochlorous acid is to pass air saturated with hydrochloric acid through a hot saturated solution of potassic permanganate acidulated with sulphuric acid. The distillate is a dilute solution of hypochlorous acid formed by the direct oxidation of hydrochloric acid, $2HCl + O_2 = 2HClO$.

3.—Hypochlorous acid is also produced when chlorine is passed into water in which finely powdered chalk is suspended; the calcic carbonate is converted into calcic chloride with evolution of carbonic anhydride, whilst hypochlorous acid remains in solution:

$$\underset{\substack{\text{Calcic}\\\text{carbonate.}}}{CaCO_3} + \underset{\text{Water.}}{OH_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Hypochlorous}\\\text{acid.}}}{2HClO} + \underset{\substack{\text{Calcic}\\\text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Carbonic}\\\text{anhydride.}}}{CO_2.}$$

On distilling the liquid a dilute solution of hypochlorous acid passes over, whilst calcic chloride remains behind.

4.—On saturating an aqueous solution of bleaching powder with chlorine, calcic chloride and free hypochlorous acid are produced:

$$\underset{\substack{\text{Calcic}\\\text{hypochlorite.}}}{Ca(OCl)_2} + 2Cl_2 + 2OH_2 = \underset{\substack{\text{Hypochlorous}\\\text{acid.}}}{4HClO} + \underset{\substack{\text{Calcic}\\\text{chloride.}}}{CaCl_2.}$$

The excess of free chlorine may be removed by passing a current of carbonic

anhydride through the liquid, and the hypochlorous acid separated from the calcic chloride by distillation. A solution of baric hydrate may also be employed, the reaction being

$$\underset{\text{Baric hydrate.}}{BaH_2O_2} + 2Cl_2 = \underset{\text{Hypochlorous acid.}}{2HClO} + \underset{\text{Baric chloride.}}{BaCl_2}.$$

Properties.—In a concentrated form the solution of hypochlorous acid is very unstable, being rapidly decomposed on exposure to the light; bubbles of chlorine escape, and chloric acid is formed; it acts as a powerful oxidizing agent, attacking the skin and turning it brown. Charcoal, iodine, sulphur, selenium, phosphorus, arsenicum, and finely powdered antimony, rapidly decompose a solution of hypochlorous acid, and are converted by it into carbonic, iodic, sulphuric, selenic, phosphoric, arsenic, and antimonic acids respectively: if the solution be concentrated, the action is sometimes attended with explosion. Iron filings are also immediately oxidized with evolution of chlorine: silver is converted into chloride whilst oxygen is liberated, and copper and mercury combine with both the oxygen and the chlorine, furnishing oxychlorides. The contact of argentic chloride with the solution of the acid decomposes the latter, causing the separation of both oxygen and chlorine in the gaseous form, although the metallic chloride appears to undergo no alteration. The most important property of hypochlorous acid is its bleaching power, which, according to the experiments of Gay-Lussac, is twice as great as that of the chlorine which it contains. When hypochlorous acid or any of its salts is heated with hydrochloric acid in excess, a molecule of each acid is decomposed, water is formed, and 2 atoms of chlorine are liberated; $HCl + HClO = OH_2 + Cl_2$. If a fragment of sal ammoniac be suspended in a solution of hypochlorous acid, oily-looking drops of the explosive compound known as chloride of nitrogen (396) are formed.

Hypochlorous acid by its action upon the alkalies and earths, furnishes salts termed *hypochlorites*, which are readily decomposed even by such feeble acids as carbonic acid; the hypochlorous acid thus liberated exerts a bleaching action on vegetable colours. The solutions of these salts are also decomposed on gently heating them, being converted into a mixture of chloride and chlorate; $3KClO$ becoming $2KCl + KClO_3$. This change is retarded by the addition of an excess of alkaline hydrate.

(358) **Bleaching Compounds.**—If the base upon which chlorine is made to act, be a powerful one, such as an alkali or alkaline earth, the gas is absorbed, and a peculiar compound possessed of bleaching properties is produced. It is in this way

that the bleaching compounds so extensively used in the arts under the names of chloride of lime, chloride of potash, and chloride of soda are prepared.

Of these bleaching compounds, chloride of lime is the most important. It is prepared by slaking well-burnt lime, and exposing it to the action of chlorine gas in layers of 2 or 3 inches (5 or 8 centim.) in thickness, upon perforated shelves in chambers made of lead, or of Yorkshire flagstones. The chlorine must be admitted gradually, in order to prevent too rapid a rise of temperature consequent upon a quick absorption of the gas. If the heat be allowed to rise much beyond 50° (122° F.), a quantity of calcic chloride and chlorate is formed, the reaction being similar to that which occurs during the preparation of potassic chlorate (361). Slacked lime, CaH_2O_2, may in this operation be made to take up about half its weight of chlorine; but it is not possible to combine calcic hydrate in the form of powder with an entire equivalent of chlorine so as to form a compound $CaOCl_2$: the product always contains a considerable excess of lime.

A few years ago, Mr. Dunlop, of the St. Rollox Works, Glasgow, introduced a method of preparing chlorine for the manufacture of bleaching powder, by decomposing a mixture of common salt and sodic nitrate with sulphuric acid. In this operation chlorine and nitrous anhydride are evolved, whilst sodic sulphate is produced; the reaction may be traced by the equations following:

$$4NaCl + 2NaNO_3 + 3H_2SO_4 = 3Na_2SO_4 + 2Cl_2 + N_2O_3 + 3OH_2$$

Sodic chloride. Sodic nitrate. Sulph. acid. Sodic sulph. Chlorine. Nitrous anhydride. Water.

$$\left[4NaCl + 2NO_2(ONa) + 3SO_2(OH)_2 = 3SO_2(ONa)_2 + 2Cl_2 + \begin{Bmatrix} NO \\ O \\ NO \end{Bmatrix} + 3OH_2\right]$$

The mixed gases are caused to pass through a vessel containing oil of vitriol, by which the nitrous anhydride is rapidly absorbed, whilst the chlorine passes on to the lime. A current of air is made to act on the nitrous sulphuric acid, by which the nitrous acid becomes converted into nitric acid, owing to the absorption of oxygen; and the mixed acids being made to act upon fresh sodic chloride, without the addition of nitre, give rise to a similar succession of decompositions:

$$2H_2SO_4 + 2HNO_3 + 4NaCl = 2Na_2SO_4 + 2Cl_2 + N_2O_3 + 3OH_2$$

Sulph. acid. Nitric acid. Sodic chloride. Sodic sulph. Chlorine. Nitrous anhydride. Water.

$$\left[2SO_2(OH)_2 + 2NO_2(OH) + 4NaCl = 2SO_2(ONa)_2 + 2Cl_2 + \begin{Bmatrix} NO \\ O \\ NO \end{Bmatrix} + 3OH_2\right]$$

The nitrous sulphuric acid may also be at once used in the leaden chambers in the manufacture of oil of vitriol (425).

Many chemists consider both chloride of lime and the corresponding potassium and sodium compounds to contain hypochlorites of the metals, in which case they would be double salts of the hypochlorite and chloride of the metal. This, however, is

more than questionable; they are probably direct combinations of chlorine with the oxides. If the compound be supposed to be a pure chloride of lime or calcic oxydichloride, the reaction is simply an absorption of chlorine, by which the compound $CaOCl_2$ is formed; but if it be supposed that a hypochlorite is produced, the following decomposition must occur:

$$\underset{\text{Calcic hydrate.}}{2CaH_2O_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Calcic chloride.}}{CaCl_2} + \underset{\text{Calcic hypochlorite.}}{Ca2ClO} + \underset{\text{Water.}}{2OH_2}.$$

Calcic chloride is deliquescent and soluble in alcohol, but bleaching powder, when properly made, is not deliquescent, and yields scarcely any calcic chloride to alcohol, the small quantity present being probably due to hydrochloric acid carried over mechanically by the chlorine employed in its manufacture; moreover, dry carbonic anhydride completely decomposes dry chloride of lime with evolution of chlorine, whereas, from the aqueous solution, only one-half of the calcium is precipitated as carbonate by a current of the gas. It is stated by Kolb (*Ann. Chim. Phys.*, 1867, [4] xii. 266) that dry bleaching powder, prepared by saturating calcic hydrate with dry chlorine, is a definite compound, having the composition $Ca_3H_6O_6Cl_4$. This body is decomposed by water with separation of calcic hydrate, yielding a solution containing calcic chloride and hypochlorite.

$$\underset{\text{Chloride of lime.}}{Ca_3H_6O_6Cl_4} = \underset{\text{Calcic hydrate.}}{CaH_2O_2} + \underset{\text{Calcic chloride.}}{CaCl_2} + \underset{\text{Calcic hypochlorite.}}{Ca2ClO} + \underset{\text{Water.}}{2OH_2}.$$

Stahlschmidt, however (*Ding. poly. Jour.*, 1876, ccxxi. 243), states that when chlorine acts on dry calcic hydrate, water is given off, and from the results of his recent researches, he supposes that the reaction which takes place is represented by the equation $3CaH_2O_2 + 2Cl_2 = 2CaHClO_2 + CaCl_2 + 2OH_2$, a portion of the water formed subsequently acting on the compound $CaHClO_2$, and decomposing it into calcic hypochlorite and hydrate: $2CaHClO_2 = CaCl_2O_2 + CaH_2O_2$. This hypothesis, however, is not in accordance with the fact that chloride of lime prepared from dry calcic hydrate yields little or no calcic chloride to alcohol. When chloride of lime is treated with water, it is undoubtedly decomposed, yielding calcic hypochlorite which may be obtained in the crystalline state by exposing a concentrated solution to a low temperature, or by evaporating it in a vacuum (Kingzett, *Jour. Chem. Soc.*, 1875, xxviii. 404). When chlorine is passed into calcic hydrate suspended in water until the alkaline

reaction has disappeared, a clear solution is obtained containing calcic chloride and hypochlorite (Stahlschmidt)

$$2CaH_2O_2 + 2Cl_2 = CaCl_2O_2 + CaCl_2 + 2OH_2.$$

Some of the properties and reactions of chloride of lime indicate that it is calcic chloride hypochlorite, CaCl(OCl), a body intermediate between calcic chloride and calcic hypochlorite, and not a mixture of the two salts. Notwithstanding the numerous experiments which have been made, the true constitution of bleaching powder, and the nature of the reaction which occurs when dry calcic hydrate is treated with chlorine in excess is far from being satisfactorily settled.

Chloride of lime emits the peculiar odour of hypochlorous acid when exposed to the air; under these circumstances, however, it gradually absorbs carbonic anhydride, and exhales, not hypochlorous acid, but chlorine,—a circumstance which causes it to be extensively used as a disinfecting agent. Cloths dipped in an aqueous solution of the chloride, when hung up in the room to be fumigated, slowly emit chlorine for many hours, but in quantities too small to be injurious to the inmates. Commercial chloride of lime is only partially soluble in water, and always contains a slight excess of water as well as of calcic hydrate. An excess of any acid when poured upon the powder causes a free evolution of chlorine; hydrochloric and hypochlorous acids being simultaneously produced, and decomposing one another, the reaction being the following, assuming that the bleaching powder is a mixture of chloride and hypochlorite:

$$CaCl_2 + Ca2ClO + 2H_2SO_4 = 2CaSO_4 + 2HCl + 2HClO$$
$$[CaCl_2 + Ca(OCl)_2 + 2SO_2(OH)_2 = 2SO_2(O_2Ca)'' + 2HCl + 2OClH]$$

then

$$2HCl + 2HClO = 2OH_2 + 2Cl_2$$
$$[2HCl + 2OClH = 2OH_2 + 2Cl_2];$$

but if the aqueous solution be mixed with half the quantity of sulphuric or nitric acid required to neutralize the lime, dilute hypochlorous acid may be distilled off and condensed in a suitable receiver. The reaction which occurs is as follows:

Ca2ClO	+	H_2SO_4	=	$CaSO_4$	+	2HClO
Calcic hypochlorite.		Sulphuric acid.		Calcic sulphate.		Hypochlorous acid.
$[Cl_2(O_2Ca)''$	+	$SO_2(OH)_2$	=	$SO_2(O_2Ca)''$	+	$2Cl(OH)]$.

The calcic chloride taking no part in the reaction under these

conditions. (*Vide* also F. Kopfer, *Jour. Chem. Soc.* 1875, xxviii. 713.)

Chloride of lime is consumed in vast quantities in the bleaching of calico and other fabrics. The calico is well washed, and boiled successively with lime water, with very dilute sulphuric acid, and with a weak solution of caustic soda, in order to remove the weaver's dressing, and greasy and resinous matters: it is then well washed, and digested in a solution of chloride of lime, containing 2 or 2½ per cent. of bleaching powder. The effect of this solution is not, however, rendered apparent until the goods are immersed in very dilute sulphuric acid, which decomposes the chloride of lime, and by liberating chlorine within the fibres of the cloth itself, rapidly removes the colour. Still, however, it is not perfectly white. The calico is therefore washed, and a second time subjected to the action of dilute caustic alkali, to remove the colouring matter rendered soluble by the action of the chlorine: it is again passed through a weaker solution of chloride of lime, and then through dilute acid; finally it is thoroughly washed in a copious stream of water, in order to remove the last traces of sulphuric acid which would otherwise destroy the fibre.

(359) **Estimation of the Bleaching Power of Chloride of Lime.**—The commercial value of bleaching powder depends upon the quantity of chlorine which can be liberated from it by the addition of an acid; for it is this portion of its chlorine only which is available for bleaching purposes. Gay-Lussac proposed to estimate the bleaching power by measurement of the bulk of a solution of indigo of known strength which a given weight of the chlorine is able to deprive of its blue colour; and subsequently he determined the amount of available chlorine by the quantity of a standard solution of arsenious acid which could be converted by a known weight of the bleaching powder into arsenic acid. The ready solubility of arsenious acid in glycerine may be taken advantage of in preparing the standard solution; 13·95 grams being dissolved in 40 c. c. hot glycerine and diluted with water to one litre: 10 c. c. of this equals 0·1 gram of chlorine. The addition of a drop of indigo sulphate serves as an indicator; the bleaching solution being run in until the blue tint is destroyed.

A still more convenient plan has been described by Graham. It depends upon the determination of the quantity of a ferrous salt which a given weight of bleaching powder in the presence of an excess of acid can convert into a ferric salt; if ferrous sulphate be used, 2 atoms of chlorine are required for the conversion of two molecules of that salt into 1 molecule of ferric sulphate; the chlorine becoming converted into hydrochloric acid, as shown in the following equation:

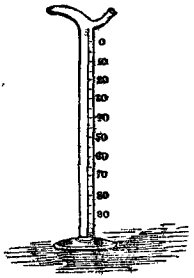
$$2FeSO_4 + 2H_2SO_4 + CaOCl_2 = Fe_23SO_4 + 2HCl + CaSO_4 + OH_2.$$

$$[2SO_2(O_2Fe)'' + 2SO_2(OH)_2 + Ca(OCl)Cl = S_2O_6(O_6Fe_2)^{vi} + 2HCl + SO_2(O_2Ca)'' + OH_2].$$

7·8 grams of crystallized ferrous sulphate require 1 gram of chlorine for its conversion into ferric sulphate. In making an experiment upon the value of

a bleaching powder, 7·8 grams of clean dry crystals of the green sulphate* are dissolved in about 60 cub. centim. of water, and acidulated with sulphuric or hydrochloric acid; 5 grams of the bleaching powder are rubbed up in a mortar with 60 cub. centim. of warm water, and transferred to a burette or tall narrow tube (fig. 292), capable of holding 106 cub. centim. of water, and graduated into 100 equal parts from above downwards. The mortar is washed with a little more water, and the washings added to the liquid in the burette, which is filled up exactly to 0°. The openings at the top are closed with the finger and thumb, and the contents of the vessel are mixed thoroughly by agitation. The solution of chloride of lime is then added gradually to the ferrous sulphate (constantly stirring the mixture), until the whole of the ferrous salt is converted into ferric salt. The progress of the oxidation is ascertained by means of a solution of red prussiate of potash, or potassic ferricyanide, K_3FeCy_6, which strikes a deep blue with the liquid if it contains any unchanged ferrous sulphate. Several drops of the ferricyanide are spotted over a white plate, and, after each addition of the chloride of lime to the solution of sulphate, a drop of the mixture is added to one of these, when a blue colour is produced. The addition of the chloride must be continued until the mixture no longer gives a blue colour with the ferricyanide. The stronger the bleaching powder, the fewer will be the number of divisions required to be poured from the burette. This number of divisions divided by 20 will indicate the number of grams of bleaching powder which contain 1 gram of available chlorine. The strength of the powder is therefore obtained by the following proportion, in which m represents the number of measures poured from the burette:

FIG. 292.



$\frac{m}{20}$: 1 :: 10 : x (the number of grams of chlorine in 10 grams of the powder);

$$\text{or } \frac{200}{m} = x.$$

Chloride of lime is frequently employed for converting a lower oxide of a metal into one of its higher oxides; indeed, a solution of chloride of lime, when mixed with hydrochloric acid, furnishes a powerful oxidizing agent. The peroxides of manganese, bismuth, cobalt, nickel, and lead, may be readily obtained by adding a neutral solution of chloride of lime to neutral solutions of the salts of these metals, and heating the liquid.

(360) **CHLORIC ACID**; *Hydric chlorate*, $HClO_3 = 84·5$, $\left[\begin{matrix}OCl\\O\\OH\end{matrix}\right]$ or $Cl-O-O-O-H$.—Chloric anhydride has not been isolated, but the corresponding acid is known. If a current of chlorine gas be passed into a solution of caustic potash (1 part of

* Ammonic ferrous sulphate cannot be conveniently substituted for ferrous sulphate, as the chlorine acts on the ammonia, and inaccurate results are obtained.

potassic hydrate, and 3 of water), it is rapidly absorbed, and a bleaching liquid is formed. This loses its bleaching properties on the application of heat, becoming converted into a mixture of potassic chloride and chlorate; 6 atoms of chlorine and 6 molecules of potassic hydrate furnishing 5 molecules of potassic chloride and 1 of the chlorate, whilst water is liberated:

$$3Cl_2 + 6KHO = 5KCl + KClO_3 + 3OH_2.$$

The potassic chlorate being much less soluble in water than the chloride, is freed from the latter by two or three crystallizations. In order to obtain chloric acid, the potassic chlorate is decomposed by hydrofluosilicic acid, which forms an insoluble potassic compound, and the chloric acid is liberated:

$$2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6.$$

Or, still better, a solution of baric chlorate is exactly decomposed by sulphuric acid. The acid solution poured off from the precipitate is concentrated by evaporation in vacuo, or over the water-bath at a heat not exceeding 38° (100°·4 F.), until it forms a syrupy liquid of a faint chlorous odour, and a powerfully acid reaction; this, however, still contains a considerable quantity of water, closely approximating to the formula $HClO_3.7OH_2$ in composition. It is instantly decomposed by contact with organic matter, and in its concentrated form it chars and even sets fire to paper. At a temperature a little above 38° (100°·4 F.), the concentrated solution of the acid undergoes decomposition, yielding oxygen gas, chlorine, perchloric acid, and water; $8HClO_3$ yielding $4HClO_4 + 2OH_2 + 3O_2 + 2Cl_2$. In diffused daylight, it gradually undergoes spontaneous decomposition. On one occasion a small specimen which had been sealed up in a glass tube was placed aside upon a shelf; but in a few weeks, although left untouched, the tube exploded in consequence of the expansive force of the liberated gases.

The metallic salts of chloric acid require a higher temperature for their decomposition than the acid itself. The action of heat upon potassic chlorate has already been mentioned as affording a very convenient source of pure oxygen (345). This salt fuses when heated to about 370° (698° F.), and at a higher temperature is ultimately converted into potassic chloride and oxygen gas; $2KClO_3$ becoming $2KCl + 3O_2$.

This decomposition also furnishes data for ascertaining the composition of chloric acid, for if a given weight of the chlorate be calcined with suitable precaution, the loss indicates the entire quantity of oxygen which it contained. The proportions of chlo-

rine and of potassium in potassic chloride being known, the composition of chloric acid is readily calculated.

(361) **Chlorates.**—Chloric acid is monobasic, the *chlorates* consequently have the general formula $M'ClO_3$. They are all decomposed by heat; oxygen is expelled, and generally a chloride of the metal is left behind, the chlorine in which can be detected by argentic nitrate. The chlorates produce scintillation when thrown upon ignited charcoal; and when heated with combustible substances, such as phosphorus or sulphur, they explode violently. It frequently happens that mere friction with these bodies is sufficient to cause a powerful detonation; for example, if half a grain (30 or 40 mgrms.) of sulphur be triturated in a mortar with 3 grains (2 decigrams) of potassic chlorate, the friction is attended with a series of small explosions. A mixture which detonates powerfully when struck or rubbed may be obtained by powdering separately equal parts of antimonious sulphide, Sb_2S_3, and potassic chlorate, and then mixing them cautiously on a card with a feather. When a fragment of a chlorate is placed in a drop of oil of vitriol, a yellow colour is produced, and the peculiar odour of chloric peroxide, Cl_2O_4, becomes apparent. Nitric acid decomposes the chlorates with formation of a nitrate and perchlorate of the metal, whilst free chlorine and oxygen escape;

$$8KClO_3 + 4HNO_3 = 4KClO_4 + 2Cl_2 + 3O_2 + 2OH_2 + 4KNO_3.$$

$$\left[8\begin{Bmatrix}OCl\\O(OK)\end{Bmatrix} + 4NO_2(OH) = 4\begin{Bmatrix}OCl\\O\\O(OK)\end{Bmatrix} + 2Cl_2 + 3O_2 + 2OH_2 + 4NO_2(OK)\right]$$

Hydrochloric acid liberates 'euchlorine' (365). Many of the chlorates are deliquescent, and they are all soluble in water, but mercurous chlorate is least so; their solutions are not precipitated by argentic nitrate. Some of the chlorates are soluble in alcohol. Paper soaked in a solution of a chlorate and allowed to dry, burns in the same manner as touch-paper. The chlorates when present in a solution, even in small quantity, may readily be distinguished from the nitrates, by adding first a few drops of a solution of indigo, and then a solution of sulphurous acid; the blue colour immediately disappears even without the application of heat, but it remains unaltered when nitrates only are present. Potassic, sodic, and argentic chlorates are anhydrous; that of barium contains 1 molecule of water, and that of strontium 5 molecules of water.

Potassic chlorate, when in solution, often affords a convenient method of converting the metallic protoxides into peroxides; for

on adding hydrochloric acid to the solution, chloric acid is set at liberty, and this exerts a powerful oxidizing action. Iron, for example, when in solution as a ferrous salt, is thus readily converted into a ferric salt on boiling.

(362) **PERCHLORIC ACID**; *Hydric perchlorate;* $HClO_4 = 100{\cdot}5$; *Density of liquid,* 1·782 at 15°·5 (60° F.).—Perchloric anhydride is unknown. If, instead of heating potassic chlorate to complete decomposition, the temperature be moderated and the process stopped when one-third of the total quantity of oxygen has been expelled, the pasty mass will be found to contain the potassium salt of an acid with a still higher proportion of oxygen, to which the name of perchloric acid has been given. The reaction appears to consist in the resolution of 2 molecules of the chlorate into 1 molecule of perchlorate, $KClO_4$, and 1 of chlorite of potassium, $KClO_2$; the latter salt being unable to exist at so high a temperature, is immediately converted into oxygen gas and potassic chloride, as follows :*

$$\underset{\text{Potassic chlorate.}}{2KClO_3} = \underset{\text{Potassic chlorite.}}{KClO_2} + \underset{\text{Potassic perchlorate.}}{KClO_4}; \text{ and } \underset{\text{Potassic chlorite.}}{KClO_2} = \underset{\text{Potassic chloride.}}{KCl} + \underset{\text{Oxygen.}}{O_2}.$$

$$\left[2\begin{Bmatrix} OCl \\ O(OK) \end{Bmatrix} = \begin{Bmatrix} OCl \\ OK \end{Bmatrix} + \begin{Bmatrix} OCl \\ O \\ O(OK) \end{Bmatrix}; \text{ and } \begin{Bmatrix} OCl \\ OK \end{Bmatrix} = KCl + O_2. \right]$$

The potassic perchlorate is readily separated from the more soluble chloride by crystallization. It dissolves freely in boiling water, but as it is much less soluble at ordinary temperatures, it crystallizes out in octohedra as the solution cools. At a red heat the perchlorate is resolved into oxygen and potassic chloride.

Preparation.—One method of obtaining perchloric acid in the form of hydrate consists in distilling potassic perchlorate with four times its weight of oil of vitriol: if the receiver be kept cool, the first portions that distil over crystallize in long silky deliquescent needles consisting of $HClO_4.OH_2$: a large proportion of the acid, however, is decomposed into chlorine and oxygen gases. According to Roscoe, the best method of preparing perchloric acid consists in boiling down a solution of chloric acid obtained by the action of hydrofluosilicic acid upon potassic chlorate. Lower oxides of chlorine escape, and an impure solution of perchloric acid is left, which, when purified by distillation, yields a heavy, colourless, thick, oily

* During the decomposition of the chlorate a considerable development of heat occurs; this may be rendered manifest by projecting a little oxide of copper or ferric oxide into the melted salt whilst it is evolving oxygen. Although neither of these compounds is oxidized in the process, they increase the rapidity of evolution of the oxygen; and the temperature of the mass rises to redness, 1 part of the salt during its decomposition evolving 39 units of heat (129,203), the combination of chlorine with potassium evolving more heat than is required for the liberation of the oxygen in the gaseous form.

liquid. If this be heated, it gives off dense white fumes. By distilling it with four times its volume of oil of vitriol, a yellow mobile fluid consisting of pure perchloric acid, $HClO_4$, first comes over. This is followed by a thick oily liquid, which is a hydrate (containing 65·8 per cent. of the anhydride), of the formula $HClO_4.2OH_2$. If this be mixed with the pure acid $HClO_4$ in equivalent proportions, it forms the white fusible crystalline substance, $HClO_4.OH_2$, already described. This crystallizable hydrate melts at 50° (122° F.), and when heated to 110° (230° F.) is decomposed into the pure acid, $HClO_4$, which distils over, whilst an oily hydrate remains in the retort, and does not come over until the temperature is raised to 203° (397°·4 F.): this has a density of 1·82, but its composition does not correspond to that of any definite hydrate.

Properties.—Perchloric acid is a colourless volatile liquid, which soon becomes yellow owing to liberation of one of the oxides of chlorine. It remains liquid at a temperature of −35° (−31° F.). It is one of the most powerful oxidizing agents known; a drop of it brought into contact with charcoal, paper, or almost any organic substance, immediately produces combustion with an explosive violence almost equal to that of the so-called chloride of nitrogen. It produces frightful burns if allowed to fall upon the skin. It cannot be redistilled without experiencing decomposition; the colourless liquid gradually becoming darker until it acquires a deep red brown tint, when it explodes. If sealed up in tubes, it gradually undergoes spontaneous decomposition, and the tubes burst from the pressure of the evolved gases. Great heat is developed when it combines with water, and if the proportion of the latter be not too large, it reproduces the white crystals of Serullas, $HClO_4.OH_2$. Dilute perchloric acid has a pure sour taste, and does not destroy vegetable colours; in this form, indeed, it is the most stable of all the acids of chlorine, dissolving iron and zinc with evolution of hydrogen gas.

Perchloric acid forms the salts known as *perchlorates*, having the general formula $M'ClO_4$: they are mostly deliquescent, and the salts of sodium, barium, and silver are soluble in alcohol. None of the perchlorates are insoluble, although the potassic salt is but very sparingly soluble, requiring 143 times its weight of water at 0° (32° F.) for solution, and 52·5 parts at 25° (77° F.). All the perchlorates are decomposed by heat, with evolution of oxygen and formation of a chloride, but they may be distinguished from the chlorates by not yielding a yellow gas when moistened with oil of vitrol.

(363) **CHLOROUS ANHYDRIDE** (Cl_2O_3=119); $\left[\begin{matrix}OCl\\O\\OCl\end{matrix}\right.$ or $Cl{-}O{-}O{-}O{-}Cl\Big]$;

Theoretic density, 4·117; *Observed density*, 4·070 (Brandau); *Mol. Vol.* [ ]; *Rel. wt.* 59·5.—Chlorous anhydride is prepared by the deoxidation of chloric

acid, this object being effected by means of arsenious acid, when the gas is required in a state of purity. Three parts of arsenious anhydride (white arsenic). and 4 of potassic chlorate are rubbed up into a paste with water, and 16 parts of pure nitric acid, of density 1·24, are added; the whole is placed in a small flask, which is filled up to the neck with the mixture, and a very gentle heat is applied by means of a water-bath (Millon, *Ann. Chim. Phys.*, 1843, [3] vii. 322). The gas must be collected by displacement in dry bottles, as it is rapidly decomposed by mercury. In this operation the arsenious acid becomes oxidized at the expense of the nitric acid; nitrous acid is formed, and this in turn is reconverted into nitric acid by decomposing the liberated chloric acid:

$$\underset{\text{Arsenious acid.}}{H_3AsO_3} + \underset{\text{Nitric acid}}{HNO_3} = \underset{\text{Arsenic acid.}}{H_3AsO_4} + \underset{\text{Nitrous acid.}}{HNO_2}$$

$$[As(OH)_3 + NO_2(OH) = AsO(OH)_3 + NO(OH)]; \text{ and}$$

$$\underset{\text{Nitrous acid.}}{2HNO_2} + \underset{\text{Potassic chlorate.}}{2KClO_3} = \underset{\text{Potassic nitrate.}}{2KNO_3} + \underset{\text{Chlorous anhydride.}}{Cl_2O_3} + \underset{\text{Water.}}{OH_2}.$$

$$[2NO(OH) + 2\begin{Bmatrix} OCl \\ O(OK) \end{Bmatrix} = 2NO_2(OK) + \begin{Bmatrix} OCl \\ O \\ OCl \end{Bmatrix} + OH_2]$$

Tartaric acid or cane sugar may be substituted for arsenious anhydride in this operation, but the gas is then mixed with carbonic anhydride.

Chlorous anhydride is a dangerous compound to prepare, as exposure to a temperature not much exceeding 55° (131° F.) is sufficient to cause it to decompose with a powerful explosion. Contact with most combustible non-metallic elements, such as sulphur, selenium, tellurium, and phosphorus also decomposes the gas with explosion; arsenicum has a similar effect. Most of the metals—including copper, lead, tin, zinc, and iron—are without action upon it, but mercury absorbs it completely. At the ordinary temperature the pure substance is a gas of a deep greenish-yellow colour; it may be condensed, however, by a powerful freezing mixture, forming a deep brown mobile liquid which boils at a little above 0° (32° F.). Its density at 0° (32° F.) is 1·330 to 1·387. Water dissolves about 10 times its bulk of the gas, or, according to Brandau (*Ann. Chem. Pharm.*, 18, cli. 340), 100 grams of water at 8°·5 (47°·3 F.) dissolve 4·766 of the anhydride, forming a deep yellow solution of *chlorous acid*, $HClO_2$. At 0° (32° F.) chlorous anhydride unites with water to form a solid hydrate of unknown composition. The solution oxidizes all the above-mentioned metals, generally yielding a mixture of chlorate and chloride, especially if the acid be in excess; for instance $2Zn + 4HClO_2 = ZnCl_2 + Zn2ClO_3 + 2OH_2$.

The following is the composition of chlorous anhydride: its combining volume, from the experiments of Millon, was formerly believed to be anomalous, the molecule being supposed to occupy 3 volumes.

		By Weight.	Millon.	By vol.
Chlorine	$Cl_2 = 71$	or 59·66 ...	60·15 ...	2
Oxygen	$O_3 = 48$	40·34 ...	39·85 ...	3
Chlorous anhydride	$Cl_2O_3 = 119$	100·00 ...	100·00 ...	2

(364) **Chlorous Acid,** $HClO_2 = 68·5$, possesses considerable bleaching power; it acts slowly upon bases, and forms monobasic salts, termed *chlorites*, of the general formula $M'ClO_2$. Potassic chlorite, $KClO_2$, is deliquescent: if its solution be slowly evaporated to dryness, it is converted into a mixture of chloride and chlorate of the metal in equivalent proportions. Sodic, baric, and strontic chlorites are also deliquescent. The chlorites are decomposed by the feeblest acids,

even carbonic acid. Plumbic nitrate produces a sulphur-yellow scaly precipitate of plumbic chlorite, $Pb2ClO_2$, when added to their solutions, which, when heated at 100° (212° F.) for a short time, decomposes with detonation. Argentic chlorite is also yellowish and insoluble.

According to Spring (*Deut. chem. Ges. Ber.*, 1874, vii. 1584), when well cooled potassic chlorite is treated with phosphoric oxychloride, a greenish-yellow gas is obtained. This is not chlorine, and is readily absorbed by water and by a solution of potassic hydrate, but without producing chlorous acid or potassic chlorite.

The chlorites may be distinguished from the hypochlorites by the addition of a mixture of arsenious anhydride and nitric acid; this does not destroy the bleaching power of the chlorites, although it does that of the hypochlorites. Their solutions deoxidize an acidulated solution of potassic permanganate.

(365) **PEROXIDE OF CHLORINE:** *Chloric Dioxide,* $ClO_2=67{\cdot}5$, or $Cl_2O_4=135$, $\left[\begin{matrix}OCl\\O\\O\\OCl\end{matrix}\right]$; *Rel. wt.* 33·75; *Theoretic Density,* 2·335; *Observed,* 2·3227; *Boiling-pt.* 9° (48°·2 F.); *Mol. Vol.* [ ].

Preparation.—Chloric dioxide may be prepared by treating fused potassic chlorate broken into coarse fragments, with two-thirds of its weight of oil of vitriol, the action being favoured by a very gentle heat. The reaction is represented by the following equation:

$$\underset{\text{Potassic chlorate.}}{3KClO_3} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Chlorine dioxide.}}{2ClO_2} + \underset{\text{Potassic perchlorate.}}{KClO_4} + \underset{\text{Hydric potassic sulphate.}}{2KHSO_4} + \underset{\text{Water.}}{OH_2}.$$

$$3\left\{\begin{matrix}OCl\\O(OK)\end{matrix}\right. + 2SO_2(OH)_2 = \left\{\begin{matrix}OCl\\O\\O\\OCl\end{matrix}\right. + \left\{\begin{matrix}OCl\\O\\O(OK)\end{matrix}\right. + 2SO_2(OH)(OK) + OH_2$$

This peroxide is also formed on heating to 65° (149° F.) a mixture of finely powdered potassic chlorate and oxalic acid; as thus obtained, however, it is contaminated with carbonic anhydride. (Calvert.)

According to Pebal (*Ann. Chem. Pharm.*, 1875, clxxvii. 1), the best method of preparing the oxide is to treat potassic chlorate with hydrochloric acid previously diluted with an equal volume of water, or a mixture of 5 parts of potassic chlorate, and 12 of sodic chloride, with sulphuric acid previously diluted with twice its volume of water:

$$KClO_3 + 2HCl = ClO_2 + Cl + KCl + OH_2.$$

The evolved gases, after being washed with a small quantity of water to remove hydrochloric acid, are dried by passing them

over calcic chloride, and condensed by means of a powerful freezing machine. The gas requires great care in its preparation, as a temperature a little above 60° (140° F.) or 63° (145°·4 F.) determines its explosion; 2 volumes of this gas furnish a mixture of 2 volumes of oxygen and 1 of chlorine, its composition being thus represented:

		By weight.		By vol.
Chlorine	Cl_2 = 35·5	or 52·59	...	1
Oxygen	O_2 = 32·0	47·41	...	2
Chloric dioxide	ClO_4 = 67·5	100·00	...	2

Properties.—This compound is gaseous at ordinary temperatures, but by slight pressure, or by exposure to a cold of −20° (−4° F.), it may be condensed to a red liquid, which, according to Millon, is liable to explode as powerfully as chloride of nitrogen. The boiling point of liquid chloric oxide, as estimated from its vapour tension by Pebal, is about 9° (48°·2 F.) at 130 millimetres pressure; a direct determination of the boiling point being precluded by the highly explosive nature of the compound. The gas is of a colour still deeper than that of chlorous anhydride, and has a similar but less irritating odour. It may be preserved unaltered in the dark, but is gradually decomposed in the sunlight into its component gases. Water dissolves about 20 times its bulk of the gas at 4° (39°·2 F.), and forms a yellow solution, possessed of powerful bleaching properties; at lower temperatures a crystalline hydrate is produced. Chloric oxide in solution is decomposed by the alkaline hydrates, forming a chlorate and chlorite:

$$2ClO_2 + 2KHO = KClO_3 + KClO_2 + OH_2.$$

Chloric dioxide acts rapidly upon mercury, and must therefore be collected by displacement. Mere contact with many combustible matters at once determines its explosion. Place, for instance, about 0·3 gram of potassic chlorate at the bottom of a tall glass, and pour upon it a little water; then having placed the glass in a deep plate, fig. 293, add a piece of phosphorus the size of a pea, and pour about 10 c. c. of oil of vitriol slowly down a long funnel reaching to the bottom of the vessel; flashes of a beautiful green light, attended with a crackling noise, will be immediately produced. If loaf sugar and potassic chlorate be

FIG. 293.

separately powdered, and mixed in equal proportions on a sheet of paper by means of a spatula, the addition of a drop of sulphuric acid will liberate chloric dioxide, which will be decomposed by the combustible matter; sufficient heat being developed to cause the mass to burst into flame, and deflagrate with great brilliancy. Peroxide of chlorine is not possessed of acid properties; alkaline solutions, however, absorb it rapidly, but when evaporated, they yield a mixture of chlorite and chlorate of the metal:

$$\underset{\text{Chloric dioxide.}}{2ClO_2} + \underset{\text{Potassic hydrate.}}{2KHO} = \underset{\text{Potassic chlorite.}}{KClO_2} + \underset{\text{Potassic chlorate.}}{KClO_3} + \underset{\text{Water.}}{OH_2}.$$

$$\left[\begin{matrix}OCl\\O\\O\\OCl\end{matrix} + 2OKH = \begin{matrix}OCl\\OK\end{matrix} + \begin{matrix}OCl\\O\\OK\end{matrix} + OH_2\right]$$

Other oxides of chlorine have been obtained, but they have no general interest; they have a composition which may be explained by considering them as compounds of chlorous anhydride with chloric or perchloride anhydride. Davy's *euchlorine*, which is evolved on gently heating a chlorate with hydrochloric acid, is a yellow explosive gas, consisting of a mixture of chlorine with chloric oxide.

CHAPTER VII.

BORON: B=11: *Triad, as in* BCl_3.

(366) **BORON** is the characteristic element of the acid contained in borax, whence it derives its name. It is always met with in nature in combination with oxygen, but in comparatively small quantities, and only in a few localities. Although one of the triad elements, it presents considerable analogy with silicon in its properties, and in its mode of combination: it may be obtained in the crystalline and in the amorphous state.

Amorphous Boron.—Boron may be obtained by the action of potassium on boric anhydride, or on potassic borofluoride. Potassic borofluoride, $KF.BF_3$, a sparingly soluble salt, is made by saturating hydrofluoric with boric acid, neutralizing the liquid with potassic carbonate, and washing the compound with cold water: it is then dried at a heat a little below redness. When cold, it is mixed with an equal weight of potassium, and heated

in a covered iron crucible, $2(KF.BF_3)+3K_2=8KF+2B$. The potassic fluoride is removed by washing with hot water containing ammonic chloride in solution.

Boron as thus obtained is an amorphous, dull olive-green powder, which, before it has been strongly ignited, soils the fingers, and is dissolved by pure water in small quantity, forming a greenish-yellow solution, from which, however, it is precipitated unchanged on adding a little solution of sal ammoniac. Boron is not oxidized by exposure to air, to water, or to solutions of the alkalies, whether cold or boiling. It is, however, easily oxidized when treated with nitric acid or with aqua regia. After exposure to intense heat in vessels from which air is excluded, it becomes denser, and darker in colour. It may be fused by the application of a heat still more intense than that required to melt silicon. As first obtained, boron exhibits a strong attraction for oxygen, and, if heated in air or in oxygen, takes fire below redness, burning with a reddish light and emitting vivid scintillations; it is thus converted superficially into boric anhydride, which melts and protects a portion of the boron. If mixed with nitre and heated to redness, it deflagrates powerfully. It is also oxidized when ignited with potassic hydrate, and when fused with potassic carbonate, it sets carbon free, and potassic borate is formed. Pulverulent boron is a non-conductor of electricity.

Boron may be obtained in the amorphous form in large quantity by the following method (Wöhler and Deville, *Ann. Chem. Pharm.*, 1858, cv. 67):—150 grams of fused boric anhydride is coarsely powdered and mixed rapidly with 90 grams of sodium cut into small pieces. The mixture is then introduced into a cast-iron crucible previously heated to bright redness; 70 or 80 grams of pulverized sodic chloride that has been previously fused are placed upon the top of the mixture, and the crucible is covered. As soon as the reaction is over, the still liquid mass is thoroughly stirred with an iron rod, and poured, whilst red hot, in a slender stream into a large and deep vessel containing water acidulated with hydrochloric acid. The pulverulent boron is then collected on a filter and washed with acidulated water until the boric acid is entirely removed; after which the washing may be continued with pure water until the boron begins to run through the filter. It must finally be dried upon a porous slab without the application of heat.

If amorphous boron is fused with aluminium, crystals are obtained, but it would seem that they are really a compound of boron and aluminium. A small Hessian crucible is lined with the pulverulent boron made into a paste with water, and the boron is pressed in strongly, as in the ordinary mode of lining a crucible with charcoal. In the central cavity a piece of aluminium weighing from 6 to 9 grams is placed; the cover is luted on and the crucible enclosed in a second, the interval between the two being filled with recently ignited powdered charcoal. The outer crucible is next closed with a luted cover, and the whole exposed for a couple of hours to a heat sufficient to fuse nickel. The temperature is then allowed to fall; and when cold, the contents of the inner

crucible are digested in dilute hydrochloric acid, which dissolves out the aluminium. Beautiful crystals are left, generally transparent, and of a yellowish-brown colour: these, however, according to Hampe (*Ann. Chem. Pharm.*, 1876, clxxxiii. 75), contain both aluminium and carbon, having a composition represented approximately by the formula $B_{48}C_2Al_3$. Their density at 17° (62°·6 F.) is 2·615. A quantity of copper-coloured, almost black, opaque plates of so-called *graphitoid* boron, a compound of boron with aluminium (Wöhler and Deville, *ibid.*, 1867, cxli. 268) are formed at the same time; they have a density of 2·5345, and they correspond closely in composition to the formula B_2Al.

Crystallized boron has a density of 2·63; it assumes the form of transparent quadratic octohedra belonging to the monoclinic system. These crystals are said to be nearly colourless when pure, but they usually contain a considerable amount of aluminium and carbon: they refract light powerfully, and are hard enough to scratch the ruby, and even sensibly to wear away the diamond. Crystallized boron does not fuse, even when heated in the flame of the oxyhydrogen blowpipe, and burns but imperfectly in oxygen when heated to full whiteness, becoming coated with a layer of fused boric anhydride. It however burns easily when heated to redness in dry gaseous chlorine, being converted into the gaseous boric trichloride. No acid or mixture of acids has any action upon crystalline boron.

Boron, like titanium, enters into direct combination with nitrogen at a high temperature; a quantity of this nitride is formed as a grey coherent mass during the preparation of crystallized boron. Pulverulent boron, when heated in a current of dry ammoniacal gas, becomes incandescent, and is converted into nitride, whilst hydrogen is liberated. Boron in all its forms burns freely in chlorine; when ignited in contact with steam, sulphuretted hydrogen, or hydrochloric acid, it decomposes them, but the latter is attacked with some difficulty; boric anhydride, boric sulphide, and boric chloride being formed respectively, whilst hydrogen is liberated.

(367) *Boric trichloride* $BCl_3 = 117·5$; *Theoretic density* 4·065; *Observed*, 4·06; *Mol. Vol.* [ ]; *Rel. wt.* 58·75.—This compound is prepared by passing dry chlorine over amorphous boron at a gentle heat, or by the action of chlorine on a mixture of boracic anhydride and charcoal heated to redness, the boric trichloride being condensed in a receiver surrounded with a frigorific mixture of ice and salt. A still better process is to heat boracic anhydride with phosphoric pentachloride at 150° (302° F.) for a long time in closed tubes, and distilling the product. It is a colourless, mobile, strongly refracting liquid, having a density of 1·35, and boiling at 18° (64°·4 F.); it fumes strongly in the air, and is instantly decomposed by water into hydrochloric and boric acids. The vapour of boric chloride rapidly attacks porcelain at a red heat, producing sililic and aluminic chlorides and aluminic borate. Its composition is the following:

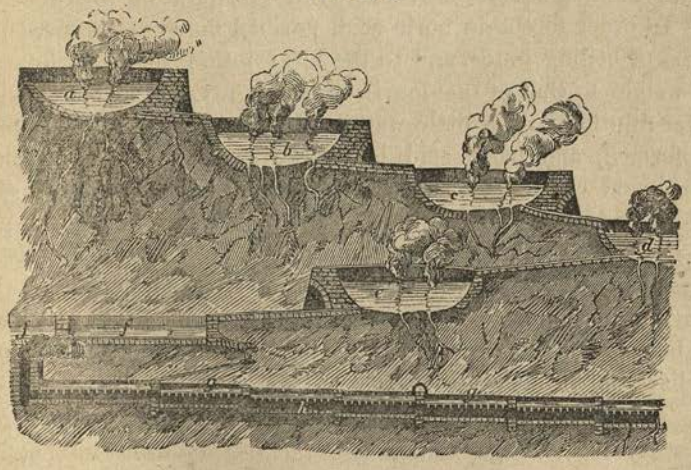
			By weight.		By vol.
Boron ...	... B	=	11	or 9·36	?
Chlorine	... Cl_3	=	106·5	90·64	3
Boric chloride	BCl_3	=	117·5	100·00	2

Two volumes of this trichloride unite with three volumes of ammonia, and become condensed into a volatile crystalline saline body, forming the *ammonio-chloride of boron*, $3NH_3.2BCl_3$.

(368) **BORIC OR BORACIC ANHYDRIDE**; *Boric sesquioxide*, $B_2O_3=70$; *Crystallized Boric acid*, H_3BO_3 or $[\mathbf{B}(OH)_3]$. —This is the only known compound of oxygen and boron. It is found combined with sodium as an acid borate in the *tincal* obtained from Thibet, and in a crystallized borate of calcium and sodium (*boronatrocalcite*, 724,) from the province of Tarapaca, in Peru, and from Africa; quite recently borax and boracic acid have been found in California, but its most abundant source is the maremma of Tuscany, where it is met with in the uncombined state, and accompanied by sulphuretted hydrogen; it issues in small quantity along with the jets of steam (*fumerolles* or *soffioni*), maintained by volcanic agency.

These, at Monte Cerboli and Monte Rotondo, in Tuscany, are directed into small lagoons or artificial basins, such as those shown in fig. 294, the waters of which, on evaporation, yield a crude boric acid, from which a large proportion of the borax of commerce is now manufactured. According to the ingenious suggestion of Lardarello, the heat supplied by the fumerolles or soffioni them-

FIG. 294.



selves is employed in this evaporation. Water from the adjacent springs is directed into the uppermost basin, *a*, which is built over a fumerolle; here it stays for twenty-four hours, and is run off after successive intervals of twenty-four hours into each of the four lower basins, *b*, *c*, *d*, *e*. From the last of these it flows into settling vats, *f*, *f*, where in the course of twenty-four hours

more the suspended matters subside. The supernatant liquid, which contains from 1½ to 2 per cent. of boric acid, is then decanted into shallow leaden evaporating pans, *g*, *g*, heated by the vapours of several fumerolles, which circulate underneath in flues, *h*, arranged for the purpose. In twenty-four hours the liquor is reduced to about half its bulk; it is then transferred to a smaller pan, on a lower level, where it is allowed to evaporate for twenty-four hours longer: it is again transferred to a smaller pan, where after the lapse of twenty-four hours more it has acquired a density of 1·07 or 1·08, and is sufficiently concentrated to crystallize on cooling. Calcic sulphate is deposited in abundance in the pans during these evaporations, and requires removal from time to time. About two thousand tons of the crude acid are thus procured annually in Tuscany. The crude acid, however, seldom contains more than three-fourths of its weight of the pure crystallized acid, the remainder consisting principally of ammonic and magnesic sulphates, with small quantities of aluminic sulphate and of other alkaline and earthy sulphates, a peculiar organic matter, and a small proportion of silica. It is recrystallized from hot water, and then dried in drying chambers heated by the fumerolles. By boring into the volcanic strata, artificial soffioni have been formed which, as at Travale, yield a large quantity of boric acid in a manner similar to that above described.

The commercial acid is purified by adding to it sodic carbonate as long as effervescence occurs, and purifying the borax thus formed by crystallization.

To obtain boric acid from boronatrocalcite, it is finely ground and dissolved in two-thirds its weight of hot hydrochloric acid. On cooling most of the boric acid crystallizes out and merely requires to be washed with cold water. The boric acid, dissolved in the mother liquors, is recovered by precipitation with lime.

In order to obtain boric acid, purified borax is dissolved in 4 parts of boiling water, and to the hot solution, oil of vitriol equal in weight to that of one-fourth of the borax employed, is added after dilution with a little water. In this process sodic sulphate is formed, and boric acid is liberated. The sparingly soluble boric acid crystallizes out on cooling, in pearly-looking scales which feel greasy to the touch. It is not, however, quite pure, as it always retains a little sulphuric acid. To remove this, the crystals are washed with ice-cold water, dried, and fused in a platinum crucible; on redissolving the mass in 4 times its weight of boiling water and allowing the solution to cool, the acid crystallizes out in a state of purity.

The following is the composition of this acid:

	Anhydride.				Crystallized: $HBO_2.H_2O$.			
Boron ...	B_2	=	22 or	31·43	B	=	11 or	56·45
Oxygen ...	O_3	=	48	68·57	$\frac{1}{2}O_2$	=	24	
Water ...					$1\frac{1}{2}OH_2$	=	27	43·55
Boric acid ...	B_2O_3	=	70	100·00	BH_2O_3	=	62	100·00

Properties.—The crystals of boric acid effloresce and lose two-thirds of their water at a gentle heat, and at a slight increase of temperature become converted into the anhydride; at a red heat, or a little below, the anhydride fuses to a transparent viscid, ductile glass, which remains clear as it cools. It gradually absorbs moisture from the air and crumbles to pieces. Its density at 15° (59° F.) is 1·4347. Boric acid communicates to its compounds the property of ready fusibility; indeed it is chiefly on this account that it is valued. Many of the borates are admirably adapted for fluxes, which are used in the glazing of porcelain, and in the melting of gold and silver.

Boric acid is sparingly soluble in cold water, requiring about 25 times its weight for solution, at 19° (66°·2 F.), but it dissolves in 3 parts of boiling water, forming a solution which has a bitterish and scarcely perceptible sour taste; if allowed to evaporate upon turmeric paper, it turns the paper brown as an alkali would do; it gives to litmus a purplish-red tint, instead of the usual bright red of the stronger acids. It gradually decomposes solutions of the carbonates even in the cold, but on the other hand, a brisk current of gaseous carbonic anhydride or of sulphuretted hydrogen will cause a separation of boric acid in crystals from a strong solution of borax. Boric acid is soluble in alcohol, and the solution burns with a characteristic green flame, which, when viewed through the spectroscope is seen to exhibit five well-marked green bands (Part I. fig. 81, No. 6). Boric acid is volatile both in the vapour of water and of alcohol, so that it is not possible to evaporate a solution of boric acid in either of those liquids without losing a portion of the acid; if steam at a high temperature be passed over boric acid or calcic borate, the acid is volatilized in considerable quantities.

Borates.—Boric anhydride is but very slowly volatilized by ignition, and hence, although its chemical activity is very feeble, at high temperatures it expels from their salts all anhydrides more volatile than itself. It enters into combination with the alkaline bases in a great variety of proportions, resembling phosphoric acid in this respect. Although many of these salts contain more than 1 molecule of acid, they all restore the colour of reddened litmus-paper. Boric acid appears to exist in three modifications; *orthoboric acid,* H_3BO_3, a tribasic acid which forms very unstable salts, the only well-defined compound being *magnesic orthoborate,* $Mg_3(BO_3)_2$; *metaboric acid,* HBO_2, obtained on heating orthoboric acid at 100° (212° F.), and *pyroboric acid,*

$H_2B_4O_7$, formed on heating the crystals for a long time at 140° (284° F.); the salts of these two acids are comparatively stable compounds. Many salts are known, however, as in the case of phosphoric acid, which have a more complete constitution. A *potassic hexaborate*, $K_2O.6B_2O_2.10OH_2$, may be obtained in crystals, and also a crystalline *triborate*, $K_2O.3B_2O_3.8OH_2$. The borates of the alkali-metals are freely soluble, those of the other metals are only imperfectly soluble; none of the borates, however, are so insoluble as to furnish an accurate mode of ascertaining the quantity of boric acid present in solution by precipitation.

All the sparingly soluble borates are dissolved by dilute nitric acid. A saturated boiling solution of boric acid attacks Iceland spar, marble, chalk, and dolomite, forming small needles of the composition $CaH_2B_4O_8.(H_3BO_3)_3$, having the same appearance as the crusts of natural calcic borate found in Tuscany on the limestone. Ditte (*Compt. Rend.*, 1873, lxxvii. 783 and 892) has succeeded in obtaining several crystallized borates in the dry way by fusing the amorphous borates with an alkaline chloride, when they are deposited in crystals on cooling; the soluble chloride is removed by washing. In this way *calcic borate*, $Ca2BO_2$, may be obtained in colourless four-sided prisms; *strontic borate*, $Si2BO_2$, *magnesic borate*, $Mg2BO_2$, and *acid baric* borates, $Ba_2B_6O_{11}$, and BaB_4O_7, (*baric pyroborate*) have also been obtained in crystals. In analysing a substance containing a borate, it is usual to determine the amount of the other acids and metals, and other constituents, and to estimate the deficiency as boracic acid. It is not unlikely that boric acid may have been overlooked in many minerals, as its detection in small quantities is rather difficult except by the aid of the spectroscope. If a borate be fused with a little hydric potassic sulphate mixed with a fourth of its weight of finely powdered fluor-spar on a platinum wire in a Bunsen gas-flame, its transient green light is easily analysed by the prism.

CHAPTER VIII.

CARBON—CARBONIC ANHYDRIDE—CARBONIC OXIDE.

§ I. CARBON: C = 12.

(369) **CARBON.**—*Density as diamond, 3·33 to 3·55; Vapour density unknown; Dyad in* CO; *Tetrad, as in* CO_2, *and* CH_4.—Carbon is an elementary body of the greatest importance. In

the diamond it is found nearly in a state of purity; with a larger proportion of foreign admixture, it occurs in the form of graphite, and still less pure in the abundant deposits of pit coal. It is also met with in enormous quantities in combination, under a variety of forms. Independently of that which exists diffused through the atmosphere in the state of carbonic anhydride, it enters into the composition of the numerous varieties of calcic and of magnesic carbonate, constituting nearly an eighth of the entire weight of calcic carbonate, and more than a seventh of that of magnesic carbonate. It has also been found in meteorites both in the free and the combined states. It is the characteristic ingredient of all substances which are termed *organic*—that is, of substances which are produced directly or indirectly from the vegetable or animal creation. The solid parts of plants, shrubs, and trees, owe their form and solidity to this element, which is mainly supplied to them from the carbonic anhydride in the atmosphere. This action of plants upon carbonic anhydride is one of the means ordained for preserving uniformity in the composition of the air. The quantities of carbonic anhydride poured forth from the bowels of the earth, and derived from the processes of respiration and combustion, and from numerous other less apparent sources, might by degrees occasion an injurious accumulation of the gas, but for this compensating action. In solar light, the leaves of plants decompose both carbonic anhydride and water, appropriating the carbon and hydrogen for their own growth and nutrition, whilst a large proportion of the oxygen which these compounds contained is returned into the air in the gaseous state. Thus the carbonic anhydride poured out by animals as a refuse and poisonous product, supplies food and sustenance to the vegetable world, which in its turn converts the carbon into a form suitable for the maintenance of life in animals. Each great division of animated nature is thus seen to be essential to the well-being and even to the support of the other. The fuel which has been burned and dissipated in vapour is again reduced to the solid state, and by the agency of vegetable life, it is once more fitted for combustion, and made a depository of fresh energy derived from the sun. Plants are, in fact, the grand agents by which, under the influence of the chemical actions of the sun's rays, deoxidization is effected, whilst animals are the channels through which recombination with oxygen is unceasingly produced, so that carbonic anhydride is the chief instrument by which the force proceeding from the sun as light and heat becomes available on the earth's surface.

(370) **Diamond,** *Density* from 3·33 to 3·55.—Carbon is found in its purest state in the *diamond,* which occurs crystallized in forms belonging to the regular system. These crystals are generally derived from the octohedron, with a cleavage parallel to each of the planes of the octohedron; the faces are often convex, and the edges are generally rounded, or *lenticular,* as they are termed, in such crystals. Diamonds usually present themselves under the appearance of semi-transparent rounded pebbles, enclosed in a thin brownish opaque crust. The gem, when freed from this coating, is generally colourless; such specimens are the most prized; it is, however, met with of various tints, the more common of which are yellow and different shades of brown, although green, blue, and rose-coloured diamonds are occasionally found. The most famous diamond mines are those of Golconda and Bundelcund in India, of Borneo, of the Brazils, and the recently discovered diamond fields at the Cape of Good Hope. The origin of the diamond is entirely unknown; it is improbable that it was formed by crystallization after fusion, since intense heat reduces the diamond to the form of graphite, and the circumstances under which it is found in nature affords no clue to the process of its formation. They have been found imbedded here and there in a fine-grained quartzose rock (*Itacolumite*) in Brazil, but with few exceptions the gem is found scantily in an alluvial matrix consisting chiefly of sandstone and rolled quartz pebbles, from which diamonds are extracted by washing and careful sorting.

Diamond is the hardest body known (crystallized boron approaching it most nearly in this respect), and is cut and polished by employing its own powder for the purpose. The fine diamond dust used for this object, after mixing with a little olive oil, is spread over a revolving steel plate, and the diamond, cemented into a suitable support, has each of its faces in turn presented to the flat face of the disk.

The Kohinoor diamond, which was cut in 1852, for the Queen, was imbedded in a copper vessel of about the size of a teacup, into which it was cemented with a mixture of equal parts of tin and lead. When it was necessary to change the position of the gem, the solder was softened by immersing the cup, with the diamond imbedded, in a charcoal fire, and heating the metal till it assumed a consistence resembling that of wet sand; in order to cool the diamond more quickly, it was plunged first into warm water and then into cold water; the cutting was effected by means of a cast-iron wheel revolving on a vertical axis about 2400 times per minute; the diamond rested upon the upper surface of the wheel, being held in its position by a kind of vice, and the pressure against the revolving disk was increased or diminished by adding or removing weights. From time to time the face of the diamond was touched with a hair pencil dipped in a cream of diamond dust and oil.

The most important use to which the diamond is applied is the cutting of sheets of glass, but only the natural face of the crystal can be employed for this purpose, crystals with curved faces being the best; they are set in a convenient handle, and in cutting, a line is traced with the diamond across the glass in the proper direction; slight pressure on each side of the cut then determines the fracture along the mark made by the diamond. A true cut is effected by such a diamond if properly used, but a diamond with angles obtained by cleavage produces only a superficial scratch with ragged edges.

The diamond has a very brilliant lustre and a high refracting power; it is a non-conductor of electricity. After exposure to sunshine, many specimens emit a feeble phosphorescent light, which may be seen in a darkened room. In vessels from which air is excluded, it may be heated intensely without change. If it be suspended in a cage of platinum wire, heated to bright redness, and then plunged into oxygen gas, it will burn with a steady red light, and with the production of pure carbonic anhydride. The diamond, however, is not perfectly pure carbon: it always leaves a minute yellowish ash, which has been found to contain silica and ferric oxide. This ash has generally the form of a cellular network, and may perhaps, at some future time, assist in determining the origin of this valuable gem. No heat hitherto applied suffices for the fusion or volatilization of the diamond, or indeed of carbon in any of its forms, although in the intense heat of the voltaic arc, it appears to be mechanically transported from one electrode to the other (280). When the diamond is introduced into the flame of the voltaic arc, it undergoes a remarkable change; as soon as it becomes white hot it begins to swell up, loses its transparency, suddenly acquires the power of conducting electricity, becomes specifically lighter, and is converted into a black opaque mass, resembling coke. The density of a diamond thus altered was 2·6778; whilst in its crystalline condition it was 3·336 (Jacquelain, *Ann. Chim. Phys.*, 1847 [3], xx. 467). The heat of the oxyhydrogen jet was found to be insufficient to produce this change.

(371) **Graphite**, or **Plumbago** (*Density* from 2·35 to 2·15) is a second form in which carbon occurs native. Its once celebrated mine at Borrowdale is now exhausted. It is likewise found in Ceylon, and in several parts of the United States, and in Bohemia and Styria, always in rocks belonging to the earliest formation. It has also been met with abundantly in the Batougal mountains, near the frontier of China, in South Siberia. The Borrowdale graphite occurs in clay slate; in other localities it is imbedded in gneiss, mica slate, or granular limestone. Graphite occurs either massive or in six-sided crystalline plates belonging

to the rhombohedral system. Carbon, in the two forms of diamond and plumbago, offers an excellent instance of dimorphism; the properties which it displays in these two states are as widely different as those of any two dissimilar elements. Graphite has a metallic, leaden-grey lustre, whence its familiar name of *black-lead*. It is very friable, feels unctuous to the touch, and leaves traces on paper upon which it is rubbed. The particles of which graphite is composed are, however, extremely hard, and they rapidly wear out the saws employed to cut it. It appears to exist in two distinct modifications, one of which, like the Borrowdale graphite, is fine-grained and amorphous; the other, like the Ceylon variety, is composed of small flat plates, united by a cementing material; this form of graphite generally occurs in a matrix of quartz (Brodie). Graphite is an excellent conductor of electricity. It is never met with in a state free from foreign admixture: the purest specimens when burned in oxygen leave from 2 to 5 per cent. of ash, which generally contains quartz, and oxides of manganese and iron; these bodies, however, are merely accidental impurities. The fine-grained amorphous graphite is highly prized for the manufacture of lead pencils: where pieces of sufficient size can be obtained they are sawn into thin slices, and these again into small rectangular prisms, which are placed in cedar wood for use. It has been found that the small fragments and the fine powder, if of good quality, may be again reduced into coherent plates by subjecting it to enormous pressure, and may thus be fitted for the manufacture of the best pencils. Black-lead is extensively used for the lubrication of machinery, and as it is quite unaltered by exposure to the weather, it forms a serviceable coating to protect coarse iron work from rust. An application of graphite which is of some importance to the chemist, is its use in the manufacture of what are termed black-lead crucibles, or blue-pots: the clay employed for this purpose is mixed with a coarse kind of graphite, and the pots made from this mixture are much less likely to crack when heated than those made of fire-clay only.

Brodie (*Ann. Chim. Phys.*, 1855 [3], xlv. 351) has described a method of obtaining graphite in a state of purity, and in a very finely divided form, which is now largely used for glazing gunpowder. It consists in mixing coarsely-powdered graphite with a fourteenth of its weight of potassic chlorate; the mixture is introduced into an iron pot, and diffused through a quantity of concentrated sulphuric acid, equal to twice the weight of the graphite employed. The mixture is heated over a steam bath as long as any peroxide of chlorine is disengaged; it is then allowed to cool, thrown into water, and washed thoroughly. It appears that during this treatment the graphite becomes oxidized, and that a new compound of carbon, hydrogen, and oxygen is formed, which enters into

combination with the excess of sulphuric acid.* If this product be now dried, and heated to redness, it gives off gas, increases greatly in bulk, and becomes reduced to an exceedingly fine powder. In cases in which the graphite was originally mixed with silica, this impurity may be got rid of by adding a small quantity of sodic fluoride to the mixture of graphite with potassic chlorate and sulphuric acid; the silica is then expelled in the form of silicic fluoride. Graphite may also be purified by repeated treatment with fused potassic hydrate, nitro-hydrochloric acid, and hydrofluoric acid.

On the behaviour of the different varieties of carbon, under the influence of a mixture of potassic chlorate and nitric acid, Berthelot has founded a process for the analysis of carbon. Diamond is not affected by the mixture; graphite is changed into graphic acid (the *graphitic oxide* of Berthelot), which by heating swells up to the black powder, *pyrographitic oxide;* the amorphous varieties of carbon are dissolved, brown solutions being produced.

The graphitic modification of carbon may be obtained artificially by several processes. When cast iron is melted in contact

* This oxidized substance may be obtained in a state of purity by the following process (*Jour. Chem. Soc.*, 1859, xii. 261):—One part of finely-powdered Ceylon graphite is intimately mixed with three parts of potassic chlorate, and enough fuming nitric acid to render the mixture fluid; the whole is then exposed for three or four days to a heat of 60° (140° F.) on a water bath. The residue must be well washed with water, dried, and subjected four or five times to the same treatment. Exposure of the mixture to the direct rays of the sun abridges the time required. *Graphic Acid*, $C_{11}H_4O_5$, as this compound is termed by Brodie, forms yellow silky plates, which are insoluble in water and in acids, but according to Stingl (*Deut. chem. Ges. Ber.*, 1873, vi. 391) it is only crystalline when prepared from foliated or crystalline graphite. It is slowly attacked by ammonia and by potash, the ammonia combining with it and forming a gelatinous body which is decomposed by acids, with separation of a white gelatinous mass.

When graphic acid is exposed to a temperature of between 260° and 320° (500° and 600° F.), it undergoes decomposition with almost explosive violence, accompanied by an evolution of heat and light; gas is given off, and an exceedingly bulky, flocculent, sooty-looking substance is left, which still retains both oxygen and hydrogen. If the graphic acid be cautiously heated in paraffin oil to a temperature of 270° (518° F.), the hydrocarbon becomes of a deep red colour, and the acid at the same time gives off water and carbonic anhydride, leaving a substance of graphitoid appearance, consisting of $C_{22}H_2O_4$; if this new body be further heated in an atmosphere of nitrogen, water and carbonic oxide escape, leaving a residue containing $C_{66}H_4O_{11}$. Even if heated to redness in nitrogen, it retains a portion of oxygen and hydrogen, giving off water, carbonic anhydride, and carbonic oxide.

Brodie considers that in these compounds the graphite retains its allotropic state, which he terms *Graphon*, and that it possesses in this form a combining number of 33, with the symbol Gr. If this be so, graphic acid $C_{11}H_4O_5$ might be represented as $Gr_4H_4O_5$, the first residue $C_{22}H_2O_4$, as $Gr_8H_2O_4$, and the second $C_{66}H_4O_{11}$, as $Gr_{24}H_4O_{11}$; graphic acid being regarded by Brodie as analogous to the hydrated oxide of silicon $Si_8H_4O_5$ discovered by Wöhler and Buff.

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with an excess of charcoal, it takes up a considerable quantity of it, and on being allowed to cool slowly, the carbon crystallizes out in the six-sided plates peculiar to graphite. Gas carbon is easily converted into graphite when heated in the electric arc, a battery of 24 elements being sufficient according to Bettendorf (*Arch. Pharm.* [2], cxliv. 79). If the battery be of sufficient power, and the heat long continued, all kinds of carbon are said to undergo this transformation into graphite.

(372) **Gas Carbon.**—In the manufacture of coal-gas those parts of the retort which are exposed to the highest temperature, partially decompose the gas as it escapes; a portion of the carbon which it held in combination is deposited, and by degrees a layer of very dense carbon is formed, having a lustre resembling that of a metal, but containing some hydrogen. The density and appearance of this mass vary according to the temperature and the pressure of gas in the retorts in which it has been produced. This form of carbon, however, is not a true graphite, as it does not yield Brodie's graphic acid when treated with potassic chlorate and nitric acid.

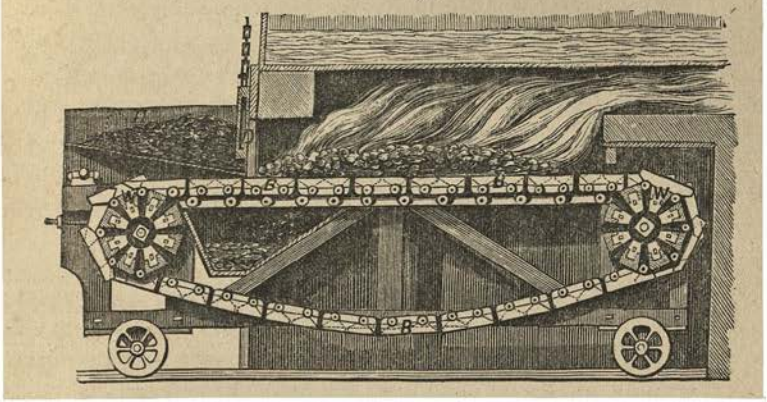
(373) **Coal.**—*Pit Coal* is a substance originally of vegetable origin, which is supposed to have assumed its present appearance and composition by the combined action of heat and moisture under great pressure. The composition of coal varies considerably according to the extent to which these decomposing actions have advanced: but, like vegetable matter in general, the different varieties of coal in all cases consist of carbon, hydrogen, and oxygen, with a small proportion of nitrogen; and in addition, it contains a variable quantity of the saline and earthy substances, which always exist in the juices of plants, besides a variable amount of iron pyrites or ferric disulphide, FeS_2. These saline matters are left, when the coal is burnt in an open fire-place, and constitute the ashes; whilst the carbon and hydrogen are entirely converted into carbonic anhydride and water, if an adequate supply of oxygen from the air be furnished: but the burning of coal, even in an open fire, is never complete, so that it gives off a quantity of gaseous and tarry matters, holding finely divided carbon or soot in suspension.

Anthracite and *Steam Coal.*—These are two varieties of coal, very similar to one another, which are much more dense and hard than ordinary pit coal, especially the former. Anthracite burns without emitting smoke, and when heated gives off but little volatile matter, as the proportion of the carbon to the hydrogen is much greater than in pit coal.

(374) **Consumption of Smoke.**—When a quantity of fresh coal is thrown upon a hot fire, the coal immediately begins to undergo decomposition, various compounds of carbon with hydrogen being abundantly evolved in the form of gas or vapour; a portion of these hydrocarbons immediately takes fire and burns with a bright luminous flame, but a large proportion of these bodies, on coming into contact with the glowing embers, is more or less completely decomposed, the carbon and hydrogen experiencing a separation from each other; the hydrogen, which is the more combustible element, becomes burned, or, if the supply of oxygen be inadequate, it passes off in the gaseous form, whilst the carbon, owing to the minute state of subdivision of its particles, is carried up the chimney suspended in the current of heated gases. By proper care, however, the volumes of black smoke ordinarily poured forth from the chimneys of our houses and factories may be prevented, whilst at the same time a considerable saving of fuel will be effected.

The principles involved in the prevention of smoke are—1st, the supply of fuel in small quantity at a time, taking care to maintain a strong, steady fire, in order that the gases may be burned as fast as they are generated; and, 2nd, the supply of an adequate quantity of atmospheric air. The latter condition is not so easily accomplished in the furnaces of the manufacturer as might be supposed. The regulated supply of fuel in small quantities may obviously be insured by due care on the part of the stoker, but it requires more labour and attention than is

FIG. 295.



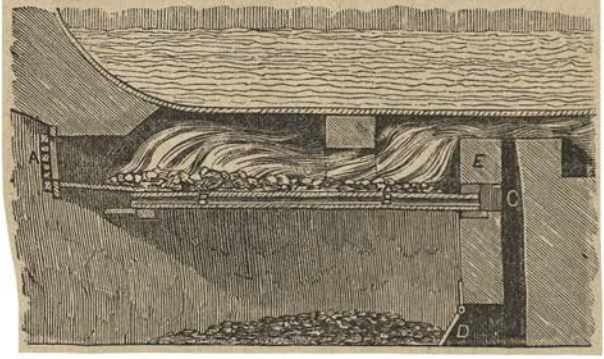
usually bestowed by him. On this account various contrivances have been from time to time invented for effecting the prevention of smoke; one class of these having for their object the regular supply of fuel by mechanical means, as is proposed by Juckes's apparatus, the essential points of which are shown in section in fig. 295.

The fire-bars, B, B, in this case consist of a series of endless chains, which are carried very slowly forward by machinery connected with the toothed wheels, W, W. A continuous but very gradual supply of fuel is furnished from the hopper, H, in front of the furnace, and the amount of coal thus admitted is regulated by raising or lowering the door, D. This apparatus fulfils its object well, but the wear and tear of the fire-bars is considerable.

In another class of smoke-burning contrivances, the object is to burn the smoke which is formed in small quantity, by supplying air at a high temperature to the unburnt gases as they escape from the fire-place. Fig. 296 represents in section the plan adopted by Mr. F. C. Hills for attaining this object.

The coal is thrown into the fire by hand, but in moderate quantities at a time; the fire-door, A, being perforated for the admission of air. The fire-bars, B, B, are tubular, and allow the passage of air into the channel, C, which opens into the chimney just behind the bridge, E, of the fire-grate; the air becomes heated as it passes through the tubular bars, and, if the quantity thus admitted is not sufficient to complete the combustion of the unburned gaseous products as they escape, more air can be supplied from below by raising the damper, D.

FIG. 296.



(375) **Coke.**—When the coal is heated in long closed iron cylinders, so constructed as to exclude atmospheric air, but to allow free escape for volatile matters, a large quantity of gaseous substances, containing the oxygen, hydrogen, and nitrogen, with a part of the carbon of the coal, passes off, whilst the greater proportion of the carbon remains behind, and constitutes *coke*, which is the only one of the products that will be noticed at present. Coke is, chemically, the same substance as the graphite deposited from the gas, but in a less pure form, owing to the earthy matters which are mixed with it. As a fuel, coke is often to be preferred to coal, since it burns without emitting any visible smoke; it has also the advantage of not swelling or caking together when heated, and thus the danger of choking the draught is avoided. The higher the temperature to which coke is exposed during its manufacture, the more dense does it become, and the better is it fitted for producing a steady and intense heat, when burned as fuel; although, unless the supply of air be tolerably abundant, it burns less freely in this dense condition than when less compact. In order to furnish a coke suited for the use of locomotive engines, it is customary to construct coke ovens, which are usually built of brick, and lined with fire-bricks, the walls being from 2 to 3 feet (6 to 9 decimetres) in thickness, in order to economize the heat; and for the same reason, several ovens are usually built together in one continuous piece of masonry. One of these ovens, 12 feet (3·7 metres) in internal diameter and 4 feet (1·24 metres) in height, will convert $3\frac{1}{2}$ tons (or about 3500 kilog.) of coal into coke in forty-eight hours.

The oven has a sliding door in front, for the purpose of introducing and withdrawing the charge, and for regulating the admission of the air, which plays over the surface of the heap and burns off the volatile matters before their escape by a short chimney. The combustion proceeds gradually, from above downwards: in about forty hours after commencing the operation, the door is completely closed, and the furnace left for five or six hours; at the end of that time the coke is withdrawn and quenched with water. A bituminous coal, like the Newcastle coal, furnishes in this way a very dense lustrous coke, which splits into long columnar masses or prisms, as the temperature in the oven gradually falls when the door is closed. A fresh charge is introduced into the oven while its walls still remain red hot. The coke is never melted in this operation, and the appearances of fusion which it frequently exhibits are due to the liquefaction, by heat, of the bituminous portions of the coal before they have undergone carbonization. A very pure form of carbon is frequently observed in the fissures of the mass, in the form of black fibres, closely resembling horsehair in appearance.

Coke may also be prepared, although with less advantage, by a smothered combustion of the coal in heaps, in a manner similar to that practised in making charcoal. Coke is subject to great variation in appearance and bulk, depending on the kind of coal employed in producing it: it is, however, nearly always more bulky than the coal that yields it.

(376) **Charcoal: Amorphous carbon.**—Carbon also exists in a third form, distinct from that of graphite, and in this state it is amorphous, or entirely destitute of crystalline structure. *Lamp-black* is an impure variety of this kind of charcoal, which always retains a portion of some incompletely burned compounds of carbon and hydrogen; it is largely manufactured by heating, in an iron pot, vegetable matters rich in carbon, such as resin or tar; the vapours thus disengaged are kindled, and burned in a current of air insufficient for their complete combustion; the hydrogen which these bodies contain, being the more inflammable ingredient, burns off first, leaving the carbon in the form of a very finely-divided powder, such as that which constitutes the visible portion of smoke. The smoky products of this imperfect combustion are made to pass through a large chamber, the walls of which are covered with coarse cloth, and here the lampblack is deposited. The purest form in which finely-divided carbon can be obtained for chemical purposes is furnished by passing

the vapour of oil of turpentine or of ether slowly through tubes maintained at a full red heat; a fine powder of charcoal is deposited within them, but this, also, even if again heated intensely in closed vessels, always retains traces of hydrogen; it may, however, be rendered almost pure by strong ignition in a current of chlorine.

Tinder is another variety of carbon in the amorphous or non-crystalline form; but the most important variety is *Wood Charcoal,* which is largely manufactured by heating billets of wood to dull redness in cast-iron cylinders, set in a furnace either vertically or horizontally, and provided with a tightly fitting lid at one end. The best plan consists in enclosing the wood to be charred in a second lighter case; this can be easily introduced into and withdrawn from the fixed cylinder, which is set in masonry, and protected from the direct action of the flame by a casing of fire-brick. From this kind of iron retort proceeds a tube connected with a condensing apparatus, where the liquid products of the decomposition may be arrested, whilst the uncondensed gases pass on, and are directed into the fire-place, in which they are consumed. After the heat has been continued for four or five hours, the end of the outer cylinder is removed, the inner case with its charge is withdrawn, and the whole, whilst still red hot, plunged into an extinguisher or iron case, provided with a tightly fitting lid, which protects it from the action of the air; in this condition it is left to cool gradually.

When wood is placed in a porcelain tube and the vapour of carbonic disulphide or wood spirit passed over it at a low temperature until the air is entirely expelled, and the tube then steadily and gradually heated to redness for about an hour, the wood is converted into a kind of coke which gives a sonorous metallic ring when struck, and is an excellent conductor of heat and electricity.

In countries where wood is abundant, the charcoal is manufactured in a comparatively rude manner. A plot of ground is levelled in or near the forest, a stake is driven into the ground, and a quantity of brushwood having been placed round its base, logs of wood are piled up regularly round the stake so as to form a mound, which is partially covered up with powdered charcoal, leaves, turf, and earth; the heap is then fired by introducing lighted fagots into an aperture left at the base of the mound for that purpose: large quantities of moisture are presently exhaled, and when the whole mass is thoroughly ignited, it is still more closely covered up, the workmen regulating the admission of air

as circumstances require; it is then allowed to burn out. When quite cold, the earth employed to stifle the combustion is removed, and the charcoal is fit for use. The combustion of one part of the wood is thus employed as a source of heat for charring the rest. Charcoal prepared in this manner is, for the purposes of fuel, preferable to that made in cylinders; it is denser and more completely deprived of volatile matters, because the heat to which it is exposed is much more intense, and is continued for a much longer period. If the diameter of the heap be 10 metres or more, the operation is not complete in less than a month. A slow combustion is found to yield more charcoal than one which is rapidly effected. The resulting charcoal retains the form of the wood, but it is much reduced in size, being generally not more than three-fourths of the bulk of the wood, and never exceeding one-fourth of its weight.

Experience shows it to be much more economical to employ dry wood in the preparation of charcoal, than wood in its green condition. Karsten found that 100 parts of recently felled wood, by drying at 100° (212° F.), lost 57 parts; by raising the temperature to 150° (302° F.) the loss upon the original weight amounted to not less than 67 parts; and the 33 parts of dry residue when charred left 25 parts of charcoal; but 100 parts of the same wood, if charred without any preliminary drying, left only 14 parts of charcoal. This remarkable difference in the amount of product depends upon the decomposing action of charcoal at a high temperature upon water, in consequence of which much of the carbon escapes in the gaseous state in the form of carbonic oxide, whilst the hydrogen of the water also passes off as gas.

The object of preparing charcoal as a fuel is to get rid of moisture and volatile matters, which, at the moment of their formation, greatly reduce the temperature of the burning mass, owing to the large amount of heat which they carry off in the latent state. Charcoal also contains in the same bulk a larger amount of carbon than the wood which furnished it, and by supplying a more compact fuel concentrates into a smaller space the heat which it emits, a condition which is often of the greatest importance in metallurgical operations demanding a high temperature.

In the economy of material to be used as a combustible, it is not sufficient to consider simply the absolute amount of heat which a given weight of the fuel emits whilst burning. The radiating power of a solid mass of fuel is much higher than that

of a gaseous combustible, but the temperature of flame is very high. A fuel which burns with flame is therefore necessary where it is needful to communicate an elevated temperature to objects at a distance from the fire-grate, or to raise large masses to a uniform temperature. Wood and bituminous coals are, consequently, particularly useful in the glass furnace and in the porcelain kiln; whilst in heating boilers, and objects in which direct radiation can act with its full effect, coke, anthracite, and coal which burns with but little flame, are especially valuable. In an ordinary open fire, these flameless coals are also the most useful, as the heat is thrown off by them into the room more completely, instead of being carried up the chimney with the gaseous products.

Charcoal never consists solely of pure carbon. According to the experiments of Violette, 100 parts of black alder (*bourdaine*) wood, charred at the following temperatures, gave amounts of charcoal progressively diminishing; but the per-centage of carbon in the residual charcoal was found to increase, as shown in the table.

Temperature of charring.		Per-centage of charcoal.	Per-centage of carbon in charcoal.
C°.	F°.		
250	482	50	65
300	572	33	73
400	752	20	80
1500	2732	15	96

A peculiar kind of imperfectly burned charcoal, of a reddish-brown colour, termed by the French *charbon roux*, is occasionally prepared for the manufacture of the gunpowder used for sporting purposes. Powder made with this charcoal absorbs moisture more rapidly than ordinary gunpowder. *Charbon roux* is procured by forcing steam, under a pressure of about two atmospheres, through a coil of heated pipe, and directing this super-heated steam, at about 280° (536° F), into the iron cylinder containing the wood, which by this means is effectually charred in the course of a few hours. The following is stated by Regnault to be its average composition in 100 parts:—

Carbon	71·42
Hydrogen	4·85
Oxygen and Nitrogen	22·91
Ash	0·82

Animal Charcoal, or ivory black, is prepared by heating bones in cylinders in a manner similar to that employed for wood charcoal, and is very largely used for decolorizing the syrups in sugar refining.

(377). **General Properties of Carbon.**—Carbon in all the forms above mentioned is chemically the same. At the ordinary

temperature it is one of those substances in which chemical attraction exhibits least activity; consequently a superficial charring is frequently resorted to with a view to protect wood from decay, as in the case of piles which are driven into mud or into the beds of rivers, to serve as foundations. For the same reason it is a common practice to char the interior of tubs and casks destined to hold liquids. Lampblack furnishes the most indestructible of black pigments, and has long been employed on this account as the basis of printing ink. The diamond is a non-conductor of electricity; in its other forms, carbon is an excellent conductor, ranking next to the metals in this respect. In a state of fine subdivision it is a bad conductor of heat, but its conducting power increases with its density. Finely divided charcoal is usually stated to have strong antiseptic powers. It certainly has a remarkable action upon putrescible substances, but Stenhouse has shown that this action consists in a rapid process of oxidation dependent upon the power which charcoal possesses of condensing oxygen within its pores. The offensive effluvia from animal matter in an advanced stage of putrefaction disappear when the putrefying substance is covered with a layer of charcoal; it continues to decay, but without emitting any odour, the carbon being dissipated as carbonic anhydride, the hydrogen as water, whilst most of the nitrogen remains as ammonia. The remarkable power possessed by charcoal in a finely divided state of absorbing various bodies, particularly colouring matters and many bitter principles (54), as well as its property of condensing a large proportion of gaseous matters within its pores (65), has been already mentioned. So rapid is this action, that Stenhouse had proposed to use a respirator filled with charcoal, to protect the mouth and nostrils in an infected atmosphere; and the employment of trays of powdered wood charcoal in dissecting-rooms, in the wards of hospitals, and in situations where putrescent animal matter is present, is found to exert a most beneficial influence in sweetening the atmosphere by absorbing and decomposing the offensive gases. These properties render charcoal a valuable material in the construction of filters, not only for decolorizing purposes, but likewise for assisting in purifying water for domestic use. Charcoal Air Filters are also extensively employed to prevent the escape of noxious vapours at the ventilating openings of sewers, as it allows the free passage of air, but condenses the offensive effluvia in its pores, where they are destroyed by a process of oxidation. It will continue active for years if kept dry.

Carbon is usually regarded as neither fusible nor volatile; but in the course of some experiments with a voltaic battery of intense energy, consisting of 600 cells of Bunsen's construction, connected so as to form a battery of 100 pairs of 6 cells each, Despretz found on operating upon carbon points in an exhausted receiver, that the vessel became filled with a dark cloud, which was deposited upon the sides of the glass as a black crystalline powder; and by exposing charcoal obtained from pure sugar, or from essence of turpentine, to the action of the battery in a small crucible of pure charcoal connected with the positive electrode, the whole of the charcoal powder became cemented into a coherent mass which had the appearance of having been fused, and possessed the properties of graphite.

At high temperatures, carbon combines rapidly with oxygen, and will remove it from a great number of its compounds, especially from the oxides of the metals; hence the various forms of carbon are very extensively employed in the reduction of these substances to the metallic condition. The deoxidizing power of carbon is sometimes exerted at the ordinary temperature of the air. Schönbein found that ferric salts may be reduced to the condition of ferrous salts, by simply agitating their solutions with charcoal powder, and the mercuric are, in like manner, converted into mercurous salts. Charcoal decomposes steam at a red heat; hydrogen is liberated, and carbonic oxide or carbonic anhydride is formed, according to the temperature at which the reaction takes place.

It had long been supposed that sulphur was the only non-metallic element besides oxygen with which carbon could be made to unite directly, and a high temperature is required in this case also to effect the combination. The experiments of Berthelot have proved, however, that by igniting charcoal intensely by means of the voltaic arc in a current of pure hydrogen, a particular hydrocarbon, acetylene, C_2H_2 is formed.

The compounds of carbon with the metals are termed *carburets* or *carbides*. Carbon also forms an extensive series of compounds with hydrogen. These hydrocarbons belong essentially to the organic department of chemistry, so that they will not be discussed here, but in Vol. III., which is devoted to the history of carbon compounds.

The simplest of these substances is light carburetted hydrogen or marsh gas, CH_4. It exists, mixed with other hydrocarbons, in coal-gas, and escapes from fissures in seams of coal in mines, sometimes in very considerable quantities.

When marsh gas is mixed with air, an explosive mixture is formed, termed by the miners *fire-damp*, which takes fire on the approach of a light, and often occasions accidents attended with loss of life to those who are engaged in coal mines. The fatal results of an explosion of fire-damp in a mine are not, however, limited to the mechanical violence which it occasions to the sufferers. The 'after-damp,' or *choke-damp* as the miners term it, or vitiated atmosphere that the explosion produces, is often fatal to those employed in other parts of the mine, or to the generous but ignorant and rash survivor who attempts to descend into the pit before it has been properly ventilated, in order to succour his comrades, or to ascertain their fate. From the composition of marsh gas, it is obvious that this gas in exploding deprives ten times its bulk of atmospheric air of the oxygen it contains, and from the deleterious nature of the resulting carbonic anhydride renders a far larger amount quite unfit for respiration.

$$\overbrace{CH_4}^{2\text{ vols.}} + \overbrace{2O_2}^{4\text{ vols.}} = \overbrace{CO_2}^{2\text{ vols.}} + \overbrace{2OH_2}^{4\text{ vols.}}.$$

The 4 volumes of oxygen which 20 volumes of air contain, produce two volumes of carbonic anhydride, and 4 volumes of steam which become condensed, leaving 16 volumes of nitrogen remaining mixed with the carbonic anhydride.

It was with a view of discovering some means of preventing these fatal results that Davy instituted those important researches on flame which led him to the invention of the *safety-lamp*, an instrument which has prevented many serious accidents, and has enabled many coal-fields to be worked which otherwise must have been abandoned, on account of the abundant escape of carburetted hydrogen from the workings.

(378) **The Safety Lamp.**—The temperature required for the combustion of different bodies varies greatly; some take fire at a very low temperature,—phosphorus, for instance, at the heat of the body; carbonic bisulphide at about 215° (419° F.); sulphur at about 250° (482° F.); others, as olefiant gas and hydrosulphuric acid, need a red heat. A high temperature is, however, essential to the existence of flames, and particularly of flames produced by the combustion of the hydrocarbons. Marsh gas, although inflammable, requires a much higher temperature to ignite it than most other inflammable bodies: it will not explode when mixed either with less than 3 or with more than 18 times its volume of atmospheric air; the gas in the latter case burns only

in immediate contact with the flame of the lamp, for the large volume of air with which it is mixed prevents the temperature from rising sufficiently high to cause the combustion to spread throughout the whole bulk of the gas: the most powerful explosion is occasioned when the gas is mixed with 7 or 8 times its volume of air.

Combustion may often be carried on below the point of inflammation. The smouldering wick of a taper recently blown out affords a case in point. Again, if a glowing coil of platinum wire, or a hot slip of platinum foil, be suspended in a current of coal-gas mixed with atmospheric air, the metal will be maintained at a red heat by the rapid combination of the oxygen with part of the hydrogen and some of the carbon of the gas, which, however, does not take fire until the platinum becomes heated nearly to whiteness.

Davy found that no explosion could be produced in a mixture of air and marsh gas, through a narrow tube, owing to the cooling influence which the tube exerted upon the gas; and the narrower the tube, the shorter was the length required to produce this protective effect. Hemming's safety-tube for the oxyhydrogen blowpipe (354) depends for its efficacy upon the cooling influence which the metallic tubes or channels, formed by the interstices between the wires, exert upon the burning jet of gas; the heat of the flame is in this way prevented from passing backwards and causing the explosion of the mixed gases in the reservoir.

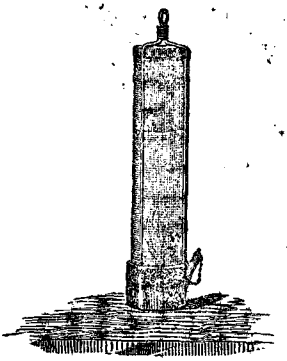
If a stout copper wire be introduced into any flame, a dark space will be observed immediately around the wire, owing to the cooling effect of the metal; a second wire cools the flame still further; and a small flame may be completely extinguished by the reduction of temperature produced by bringing down a coil of wire upon it so as completely to surround the flame; but if the same coil be previously heated to redness, and, whilst still hot, be placed over the flame, the latter will continue to burn.

By using wire gauze, we may easily cut off the upper part of a flame, the unburned gases being cooled by its means below the point of inflammation: if a piece of gauze with large meshes be employed it will cut off the flame as long as it remains cold, but the flame will traverse the network as soon as the wire becomes red hot: with finer meshes (about 64 to the square centimetre, or 400 to the square inch) the conducting power of the metal is sufficient to cool the flame below the point of ignition, even although the wire itself be red hot. In a similar manner the gas

above the gauze may be kindled, and the flame will not pass through to the gas below.

These principles were beautifully applied by Davy in the construction of his miner's lamp, which is merely an oil lamp (fig. 297) enclosed within a cylinder of fine wire gauze, provided with a double top, and with a crooked wire, w, which passes up tightly through a tube traversing the body of the lamp, for the purpose of trimming the wick without the necessity of removing the wire covering. When such a lamp is introduced into an explosive atmosphere of fire-damp, the flame is seen to enlarge gradually as the proportion of carburetted hydrogen increases, until at length it fills the entire gauze cylinder; when the gas is in sufficient excess, the lamp is entirely extinguished; if it be withdrawn from the explosive mixture while the cylinder appears to be full of flame, the wick is generally rekindled, and the lamp continues to burn in the air as usual. Whenever this pale enlarged flame is seen, the miner must withdraw; for although no explosion can occur whilst the gauze is sound, yet at that high temperature the metal becomes rapidly oxidized, and might easily break into holes, when the mixture of inflammable gas and air outside the lamp would become ignited and immediately cause an explosion of the fire damp.

FIG. 297.



The wire gauze used in the construction of these lamps contains about 121 meshes per square centimetre, or from 700 to 800 meshes in the square inch. In a strong current of air, the heated gas may be blown through the apertures of the gauze before its temperature is sufficiently reduced to prevent the explosion, but such an occurrence may be guarded against by the use of a screen, although from carelessness in using the lamp, it would appear that several very serious explosions in mines have been produced in this way.

In the laboratory, advantage is sometimes taken of the inability of flame to pass through wire gauze, in order to obtain a smokeless flame from ordinary coal-gas:—A metallic chimney, five or six inches (12 or 15 centim.) long, open below, and furnished at top with a cap of wire gauze, is placed over any convenient form of burner; the air enters at the bottom and mixes with the gas: this mixture burns above the wire gauze with a blue flame, which emits scarcely any light, and deposits no smoke upon cold objects, provided that the supply of gas be duly proportioned to that of the air which mixes with it.

This method of burning gas is now, however, entirely superseded by the use of the "Bunsen lamp" in one or other of its various forms. This lamp consists of a brass tube about 3 in. high and $\frac{3}{8}$ in. in diameter.* At the bottom, a little below the orifice of the jet, are four holes for the admission of air. On turning on the gas and lighting the lamp at the top of the brass tube, a blue conical flame is obtained, which is very feebly luminous, and does not deposit any soot on cold bodies held within the flame, provided the size and shape of the gas-jet is properly adapted to the size of the tube, and the area of the air-holes. In this apparatus, the gas issuing under pressure from the jet causes a rarefaction in the upright tube; the air consequently enters by the holes at the base, and the gas becomes mixed with air before it issues at the top of the tube, usually containing 1 vol. of gas to 2-2$\frac{1}{2}$ vols. of air. As ordinary London coal gas requires at least three times its volume of air to form an explosive mixture, the mixed air and gas burnt at the lamp gives a steady flame which has no tendency to explode and light the gas at the jet below. The smokeless nature and feeble luminosity of the flame would appear to be due in great part to the diluting action of the nitrogen of the air, for a mixture of coal gas with nitrogen, carbonic anhydride, or even steam, burns with a blue smokeless flame very similar to that of the Bunsen lamp. If the gaseous mixture is heated to redness before igniting it at the lamp (as when the upright tube is made of platinum instead of brass and heated to redness by the blowpipe), it gives a luminous flame, which deposits soot on cold bodies held in it. This effect, which is often observed in the smoky flame produced after a time when a "rose" has been placed on the top of the tube and has become nearly red hot, is probably due to the heat communicated to the gases before they are ignited together with that produced by their combustion being sufficient to compensate for the cooling effect exercised by the diluent gas. An excellent epitome of the "Theory of the Bunsen Lamp," by T. E. Thorpe, is contained in the *Jour. Chem. Soc.* 1877, I. 627.

(379) **Nature of Flame.**—It is necessary to the production of flame, that the combustible be of such a nature as to be capable of being converted into vapour before it undergoes combustion, otherwise no flame is produced. Well-burned charcoal or diamond burns with a steady glow, unattended with flame, as also does iron wire. None of these substances are susceptible of volatilization at the temperature attending their combustion. Sulphur, phosphorus, and zinc, pass into the aëriform condition before they attain a temperature as high as that generated by their combination with oxygen, and they, as well as the various combustible gases, burn with flame.

Flame is, in fact, produced whenever a continuous supply of combustible vapour or gas combines at an elevated temperature with oxygen, or with some gaseous supporter of combustion. In all ordinary cases, therefore, flame is a luminous envelope which forms a limiting surface between the unburned combustible

* This is the size usually employed in the laboratory, but much larger lamps are occasionally used, with tubes as much as 10 or 12 in. long and 1$\frac{1}{2}$ in. in diameter.

within, and the supporter of combustion without. This hollow structure of flame may be easily shown by experiment. If a wooden match be held for a few seconds across the middle of the flame of a spirit-lamp with a large wick, the match will become charred at the edges of the flame, but the intermediate portion will remain uninjured. If a fragment of phosphorus be placed in a small deflagrating spoon, ignited, and then introduced into the middle of the flame, it will be extinguished; but it will burn with its former energy the moment that the spoon is withdrawn from the flame. The tapering form which flames assume, is due to the ascending current produced in the atmosphere by the heat attendant on the combustion. Within the burning portion of the flame is an atmosphere of unburned combustible matter, as may be shown by inserting into a flame such as that of a wax candle, just above the wick, the lower extremity of a glass tube, open at both ends, about $\frac{1}{3}$ of an inch or 8 millimetres in diameter, and five or six inches (12 or 15 centimetres) long; the gases in the interior may thus be drawn off, and ignited at the upper aperture of the tube.

It is important to remark that the light and heat emitted by flames are by no means proportioned to each other. The heat is due solely to the energy of the chemical action, but it often happens that very little light is emitted, although the heat developed may be very great: the hydrogen flame, although very hot, is barely visible in clear daylight; and that of the oxyhydrogen jet itself, although one of the most powerful sources of heat at our command, is scarcely more luminous than the flame of hydrogen. The light of sulphur burning in oxygen is also feeble, notwithstanding the intense energy with which the two elements combine; and phosphorus and chlorine, although they unite so energetically as to take fire at ordinary temperatures by mere contact, yet emit but little light during their combination.

It is often stated that in all luminous flames the light is emitted from solid particles highly ignited, but undoubtedly this is not the case in every instance. The light from bodies feebly ignited is red; as the temperature rises the light becomes yellow, then white, and when the heat is very intense, the more refrangible rays of the spectrum predominate, so that it has a shade of blue or violet (89). A flame which ordinarily gives but little light may, under other circumstances, become luminous, as is seen when a mixture of chlorine and hydrogen, or of oxygen and hydrogen, is fired under pressure in the Cavendish eudiometer, although it is but feebly luminous when a jet of the mixed gas is

burned in air under the ordinary pressure: the increased intensity of the light emitted is probably a compound effect produced not only by the increased temperature, but also by the greater density of the gases combining.

By introducing a solid object into a feebly luminous flame, a platinum wire, for example, into the oxyhydrogen jet, or, better still, a body which, like lime, does not melt at that temperature, the light becomes so intense that the eye can hardly support it. Such bodies, however, since they do not contribute to the chemical changes occurring in the flame, necessarily reduce its heat, owing to their conducting power. It is immaterial whether the bodies so introduced be combustible, or have already undergone perfect combustion:—the flame of hydrogen may be rendered luminous either by blowing a little powdered charcoal through it, or by allowing finely powdered magnesia, zincic oxide, or the white fumes of phosphoric anhydride produced by the combustion of phosphorus to traverse it. An excellent illustration of this point is afforded by contrasting the painfully intense light produced by the combustion of phosphorus in oxygen, where the solid, scarcely volatile, phosphoric anhydride is produced, with the feeble light emitted by the same body as it burns in chlorine. Still, as Frankland remarks, there are cases where light of considerable intensity is emitted, although no solid particles are formed during combustion. Arsenicum, when burned in a current of oxygen, emits a sensible amount of light, although the arsenious anhydride produced is vaporized below a red heat, and sulphide of arsenic (realgar), when mixed with a suitable proportion of nitre, furnishes so intense a white light that it is used as a signal light under the name of Indian fire. In the last case, however, solid particles are produced by the combustion, potassic sulphate being among the products.

In like manner Frankland urges that carbonic bisulphide, when burned in air, furnishes a pale lambent blue flame without any sensible light, but if burnt in oxygen it produces an intensely brilliant light, and if nitric oxide be substituted for oxygen, a similar bright flash of light accompanies the rapid combustion: in this case it is certain that no solid matter is present.

It would appear that the higher the density of the combustible products of combustion, the greater the luminosity of the flame. Frankland performed some experiments which put this beyond question. Hydrogen and carbonic oxide burn in air and oxygen at the ordinary pressure with flames of very small luminosity, but under a pressure of from 10 to 14 atmospheres

the intensity of the light emitted is very considerable, the spectra of the flames being continuous from red to violet. By rendering gases incandescent by the passage of electric sparks precisely similar results were obtained, the sparks being always more brilliant in the denser than in the rarer gas. And by using atmospheric air and gradually increasing its density by a condensing syringe the sparks became brighter.

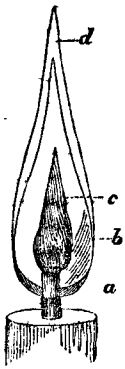
These results induce the belief that in ordinary flames used for illuminating purposes, and which are all produced by the combustion of compounds of carbon and hydrogen, the luminosity is not due to the presence of solid particles of carbon, as supposed by Davy, but to the incandescence of gaseous hydrocarbons of great density. The recent researches of Stein (*Jour. pr. Chem.* 1874 [2], viii. 402) and Heumann, (*Ann. Chem. Pharm.* 1876, clxxxii. 1: clxxxiii. 102, and clxxxiv. 206) however, tend to support Davy's hypothesis, for it has been shown that chlorine,—which, as is well known, decomposes hydrocarbons at a red heat with separation of carbon,—when introduced into a feebly luminous hydrocarbon flame increases its luminosity; also that heated surfaces as well as cold ones become covered with soot when held in a luminous flame, so that the deposit of soot does not result merely from the condensation of dense hydrocarbon vapours. This is confirmed by the fact that the soot deposited from luminous flames does not contain more than 0·9 per cent. of carbon, and cannot be vaporized again by the application of heat. Again, if a rod is held in a luminous gas flame, soot is deposited only on that surface against which the issuing gas impinges, and not uniformly on the rod, as it should be if the soot were the vapour of heavy hydrocarbons condensed by its cooling action. It is evident, therefore, that the soot cannot be the condensed vapour of those heavy hydrocarbons to which the luminosity of such flames is sometimes attributed.

The fact that ordinary luminous flames are transparent has been adduced in support of the hypothesis that they consist of gaseous matter only, but it has been shown that the luminous portion of an ordinary flame is not more transparent than the cloud or film of smoke rising from burning turpentine, or the flame of hydrogen rendered luminous by chromic oxide (by mixing it with the vapour of chromyl chloride, CrO_2Cl_2) both of which certainly contain solid particles. The most conclusive evidence, however, is afforded by the fact that although luminous flames which are free from solid matter cast no shadows on a white screen when exposed to sunlight, ordinary luminous hydro-

carbon flames, under similar circumstances, cast distinct shadows in the same way that those flames do which undoubtedly owe their luminosity to solid particles, showing that they too contain solid matters.

The flame of a candle is sustained by the decomposition of the melted wax or tallow absorbed by the wick, and its conversion into gaseous hydrocarbons by the heat of the combustion. At the lower part of the flame, *a*, fig. 298, these hydrocarbons are immediately mingled with atmospheric air, no separation of carbonaceous matter occurs here, and they burn with a pale blue light. The greater portion of the combustible gas and vapour, however, is still unburned; these vapours rise above the wick, forming the central dark part, *c*, of the flame: here they are subjected to a high temperature from the combustion of the blue portion already mentioned; some of the more oxidizable hydrogen undergoing combustion and thus giving rise to the formation of denser hydrocarbons which become intensely ignited in the burning gas, emitting light in the part marked *b*; and this carbonaceous matter itself, in a properly adjusted flame, gradually burns away without residue or smoke, as it comes to the surface, *d*, and meets with oxygen.

FIG. 298.



In order to produce the maximum amount of light when burning gas, the point which requires the greatest attention is the due adjustment of the supply of air, which must not be too limited; otherwise, as may be seen by closing the central tube which admits air to an argand burner, the light becomes red from the reduction of temperature, the carbon passes off unburned, and the oxygen being insufficient to complete the combustion, the flame becomes smoky. The light of a flame is increased by any contrivance which, without deranging the order of the combustion, concentrates it into a smaller space, so as to raise the temperature to the maximum, whilst the velocity of the current of air is moderate, so as to prolong as much as possible the time during which the vapours are maintained in the ignited state. It is in this way that an argand burner produces a far greater amount of light with a given consumption of gas, than if the same quantity of gas were burned in separate jets. If, however, the quantity of air supplied by the flame be increased beyond a certain limit, the total amount of light given out by the flame will be diminished, although its brilliancy may be increased. This may be well shown by substituting a much longer chimney for that ordinarily

used with the argand burner, so as to increase the draught and consequently the amount of air passing over the flame in a given time; under these circumstances a change will be observed in the character of the flame which, although whiter and giving a more brilliant and intense light, is diminished in size, and when examined photometrically will be found to emit less light than with a chimney of the ordinary length. If the amount of air be increased still further, the gas burns with a blue, feebly luminous flame; an effect which may be seen by blowing upon a common gas flame, or by watching the effects of the wind upon the exposed gaslights at night: a considerable increase in the pressure of the gas produces a similar effect. In these cases the gas becomes immediately mixed with the oxygen of the air, and is completely burned before it has been exposed to an elevated temperature for a time sufficiently long to allow of the separation of the carbonaceous matter. Moreover, it is cooled by contact with portions of the air which do not participate in the chemical action. If, however, the flame be supplied with heated air, as is the case in the Silber burner, a much more brilliant light is obtained without materially diminishing the size of the flame.

Frankland (*Phil. Trans.* 1861, 631) found that the rate at which candles and other similar combustibles burn, is not altered by variations in the atmospheric pressure.* Candles burned at the top of Mont Blanc at the same rate as in the valley of Chamounix; but the luminosity of the flame is greatly affected by the pressure, for the amount of light emitted by the same candle on the summit of Mont Blanc was far less than that which it produced in the valley; and by careful experiments conducted under regulated pressures, it was found that as the pressures decreased from 30 to 14 inches ($760^{mm.}$ to $355^{mm.}$) of mercury, the illuminating power gradually diminished. In a series of experiments upon the light of burning gas, Frankland found that taking the light emitted by the combustion of a given volume of gas, in a certain burner, under the ordinary pressure of 30 inches (or $760^{mm.}$) of mercury, at 100, the same volume of gas for each diminution of 1 inch in the pressure gave 5·1 less light; the diminution of light being directly as the diminution of pressure: so that at 14 inches ($355^{mm.}$) the light emitted instead of amounting to 100 was reduced to 18·4; and this rate of

* Wartha (*Jour. pr. Chem.* [2] xiv. 84) states, however, that stearine candles burn more slowly under increased pressure, a difference of from 13 to 17·5 per cent. being observed at the ordinary pressure and at 1·95 atmospheres.

diminution was found to hold good with the light of hydrocarbon flames generally.

On the other hand, the luminosity of all flames may be proportionately increased by augmenting the atmospheric pressure. So rapidly does this effect increase, that an ordinary spirit lamp which burns in the open air with scarcely any measurable amount of light, and without smoke, becomes powerfully luminous in air at a pressure of 4 atmospheres, and when supplied with air compressed still more, even burns with a smoky flame. The result of these and other carefully devised experiments led to the unexpected conclusion that the combustion of gaseous matter is rendered less perfect in proportion as the density of the atmosphere is increased; and, on the other hand, within certain limits, the more rarefied the atmosphere in which flame burns, the more complete is its combustion. No reduction in the temperature of the flame is produced by a reduction of the pressure of the surrounding air within certain limits, the observation holding good as low as 14 inches ($355^{mm.}$) of mercury. The decrease in illuminating power in a rarefied atmosphere is attributed by Frankland to the readiness with which the oxygen of the atmosphere finds access to the interior of the flame, owing to the greater mobility of the particles of the air under diminished pressure. Wartha, however, considers that the difference observed in the luminosity of flames under varying pressure, is due to the effect of pressure on the temperature at which dissociation takes place: this occurs at a lower temperature under a high pressure, than under a low pressure, so that when candles are burning in the atmosphere at a greatly increased pressure, dissociation takes place more readily than the products can be completely oxidized, notwithstanding the increased supply of oxygen, so that a smoky flame results. Under reduced pressure the converse holds good.

(380) **Theory of the Blowpipe.**—The temperature of a flame may be very materially increased by augmenting the activity of the combustion, and concentrating its effect by diminishing the extent of surface over which it would otherwise take place. It is upon this principle that all blowpipes act; a jet of air or of oxygen is thrown into the interior of a flame, whereby the combustion is rendered more rapid, it is limited to a much smaller space, and is entirely changed in character.

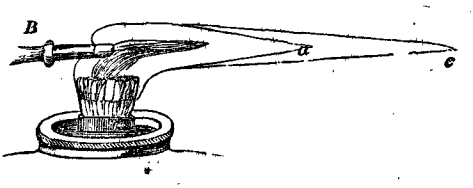
The mouth-blowpipe is one of the most valuable and portable instruments of research which the chemist possesses: he is enabled by its means, in a few minutes, to arrive with certainty and economy at results which, without its aid, would require much

expenditure both of fuel and of time; and it often affords information which could not be obtained in any other way.

The mouth-blowpipe consists essentially of a bent tube, terminating in a fine uniform jet, with a chamber for the condensation of moisture from the breath. A very convenient form of the instrument is shown at fig. 299. It consists of a conical tube of tin plate, about 8 inches (20 cm.) long, open at the narrow end, *a*, which is rounded off so as to adapt itself to the lips, and closed at its lower end, from the side of which projects a brass tube, *b*, about an inch ($25^{mm.}$) in length, upon which is fitted a small brass jet. This jet is inserted to a short depth into the flame of a candle or oil lamp, about an eighth of an inch, or $3^{mm.}$, above the wick as at B, fig. 300. When a current of air from the blowpipe is directed horizontally along the surface of the wick, the flame loses its luminosity, and is projected laterally in the form of a pointed cone, in which three parts are distinctly discernible. In the centre is a well-defined blue cone; outside that is the brilliant part of the flame, terminating at *a*, and exterior to that is a pale yellow flame, *c*. The different parts of this flame possess very different properties. The blue cone is formed by the admixture of air with the combustible gases rising from the wick, and it corresponds to the blue portion, *a*, of an ordinary flame, fig. 298. In this part of the flame, combustion is complete, and the oxygen introduced by the jet is in excess: the points where the excess of oxygen is absorbed by combination with fresh portions of the combustible vapours which are constantly rising from other parts of the wick, are clearly defined by the surface which seems to limit the blue cone. In front of this blue cone is the luminous portion, containing unburnt combustible gases at a high temperature, which of course have a powerful tendency to combine with oxygen.

Fig. 299.

Fig. 300.

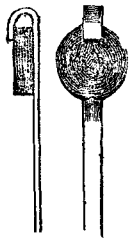


If a fragment of some metallic oxide, such as cupric oxide, sufficiently small to be completely enveloped by the luminous portion, be introduced into this part of the flame, the oxide will be deprived of oxygen, in consequence of the superior attraction of the hot gases for this element, and the oxide will be reduced to

the metallic state: hence this portion is termed the *reducing flame* of the blowpipe. At the apex, *c*, of the flame, the effects are reversed. Here, atmospheric oxygen at a high temperature is mechanically carried forward along with the completely formed products of combustion, and a fragment of any readily oxidizable metal, such as lead, copper, or tin, if placed at this point will quickly become coated with oxide; hence this spot is termed the *oxidizing flame* of the blowpipe. A good illustration of the opposite actions of these contiguous portions of the flame is afforded by the effects which they respectively produce on a piece of flint-glass tubing. The plumbic silicate contained in the glass is partially decomposed in the reducing flame, and the glass at this point becomes black and opaque from the reduction of the compound of lead to the metallic state; but by placing the blackened part for a few seconds in the oxidizing flame, oxygen is again absorbed by the metal, and the transparency of the glass is restored.

(381) **Use of the Mouth-Blowpipe.**—The art of maintaining a continual blast by the mouth-blowpipe is not easily described, but it can be acquired by practice without much difficulty. When a substance is to be examined by the blowpipe, it may be first heated alone in a small glass tube, in order to observe whether it melts or decrepitates, or is volatilized wholly or partially. It may next be heated in a narrow tube open at both ends, to ascertain whether it burns, or changes colour, or emits any odour. It should then be ascertained whether it is reduced to the metallic state, and if it be reduced, what is the colour of the metal; whether it fuses easily, or whether it is brittle, crystalline, or malleable. These observations upon reduction may be best made when the globule is exposed to the flame upon a disk of charcoal, which can be conveniently supported, as proposed by Mr. Griffin, in the manner shown at 1, fig. 301, which represents an edge view of a slip of tin plate, about 8 inches ($20^{cm.}$) long, and half an inch ($12^{mm.}$) wide, bent at one end so as to hold the charcoal disk. No. 2 shows it in front. The charcoal should be sawn into slices about the third of an inch, or $8^{mm.}$, in thickness, so as to present a surface across the grain. A small cavity should be formed upon the upper surface of each disk for the reception of the fragment of material under examination, which should be about the size of a pin's head, or a grain of mustard seed.

FIG. 301.



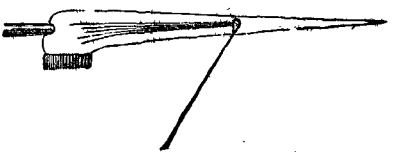
Sometimes, when the substance is not easily reducible, a platinum wire bent into a hook at one extremity forms a more convenient support, as shown at fig. 302. It may by this means be ascertained whether the substance imparts any colour to the flame; whether the body, if it be fusible, yields a transparent, an opaque, or a coloured bead; whether any change be produced in the substance, according as it is heated in the reducing or in the oxidizing flame.

The employment of certain fluxes often aids the judgment of the operator by the colour or appearance thus produced. The most important of these fluxes are borax, microcosmic salt (ammonic sodic phosphate), and sodic carbonate, or *soda*, as it is usually termed, in speaking of blowpipe reactions. When either borax

or microcosmic salt is used, a platinum wire forms the best support; but when sodic carbonate is employed, especially for the purpose of reducing the metals, a support of charcoal is required.

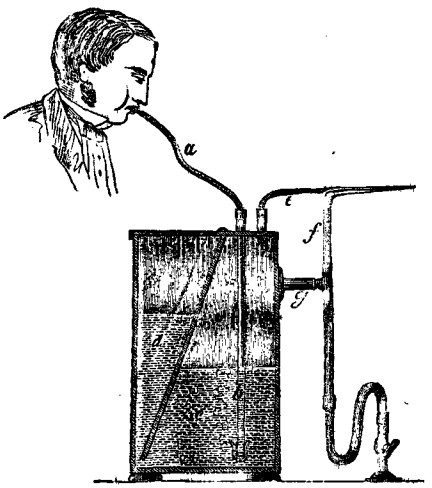
Different forms of the blowpipe have been proposed, according to the purposes for which the instrument is destined. The glass-worker requires a large supply of air to be maintained uninterruptedly for long periods, and he usually employs a pair of double bellows, worked by the foot.

FIG. 302.



A portable blowpipe for glass-working may be made as follows:—A rectangular box of zinc, fig. 303, about 14 inches ($36^{cm.}$) high, and 6 inches (or $15^{cm.}$) wide, is divided into two chambers, *c* and *d*, by a diaphragm which passes obliquely nearly to the bottom of the box; these chambers communicate with each other below; one of them, *d*, is open above, and is covered with a loose lid; the other chamber, *c*, is closed at the top; a blowpipe jet, *e*, passes just through the covering of this chamber, which is further supplied with a longer pipe, *a b*, passing down to within a short distance of the bottom, covered with a flap of silk to prevent the return of the water in case the operator should suddenly cease to blow through *a*. If the box be now partially filled with water, the pressure of the column of liquid will expel the air through the jet, *e*, in any desired direction. By blowing down the long pipe, the operator can renew the supply of air as often as may be necessary: it bubbles up into the closed chamber, *c*, driving the water back into the open one, when the column of liquid, by its pressure, renews the blast as before. The gas-burner, *f*, can be raised or lowered as may be necessary, and by means of a sliding joint, *g*, can be made to approach towards or recede from the jet, *e*, as may be required. An oil-lamp may be used when gas is not at hand; it, has, indeed, the advantage of giving a more intense heat than gas, and it is less likely to reduce the plumbic oxide contained in flint glass.

FIG. 303.



Where a very intense heat is required, a spirit-lamp or gas-flame may be employed, through which a current of oxygen is directed from a gas-holder; and occasionally, in cases where a still stronger heat is requisite, recourse may be had to the oxyhydrogen blowpipe, in which, owing to the complete intermixture of the two gases, the flame is solid, and therefore of comparatively small dimensions.

§ II. CARBONIC ANHYDRIDE: $CO_2=44$.

(382) **CARBONIC ANHYDRIDE,** *Carbonic Dioxide, or Carbonic Acid.—Molecular volume* [ ]; *Relative weight* 22; *Observed*

Density 1·5291; *Theoretic Density* 1·5224.—Carbonic anhydride was originally termed *fixed air*, from the circumstance of its having been discovered by Dr. Black, in 1757, as a solid or fixed constituent in limestone, and from its becoming fixed or absorbed by solutions of the caustic alkalies.

Many natural compounds of metallic oxides with carbonic anhydride exist, one of the most abundant of which is *carbonate of lime*, or *calcic carbonate*, which occurs in vast quantities as limestone, chalk, and marble. When this compound is heated to bright redness (which, if the result is to be accurately examined, must be effected in a platinum tube), carbonic anhydride is expelled as a colourless and transparent gas, whilst pure quicklime, or calcic oxide, is left behind; $CaCO_3$ becoming CaO and CO_2.

Preparation.—In actual practice, carbonic anhydride is obtained by a much more convenient plan. Carbonic being but a feeble acid, is expelled from its compounds by almost every other acid which is freely soluble in water; it is therefore easily separated from its salts by the addition of one of these acids. Fragments of chalk, or of marble, which is a more compact form of calcic carbonate, are placed in a retort or gas-bottle, and some powerful acid, such as nitric or hydrochloric, diluted with 8 or 10 times its bulk of water, is poured upon the chalk, when the acid exchanges its hydrogen for the calcium, producing calcic nitrate, or chloride, on the one hand, and carbonic acid, H_2CO_3, on the other: the carbonic acid at the moment of its formation breaks up into water and gaseous carbonic anhydride, the latter of which escapes with brisk effervescence. The following equation shows the nature of this decomposition when chalk and hydrochloric acid are employed;

$$CaCO_3 + 2HCl = CaCl_2 + OH_2 + CO_2.$$
$$[CO(O_2Ca)'' + 2HCl = CaCl_2 + OH_2 + CO_2.]$$

Sulphuric acid cannot be advantageously used for decomposing the calcic carbonate, as the calcic sulphate which is formed, being insoluble, serves to protect the unattacked carbonate from the acid, so that the action is greatly retarded. This inconvenience does not attach to the use of hydrochloric or nitric acid, since the calcic chloride or nitrate which is formed, being readily soluble, is at once removed.

Limestone, Iceland spar, oyster-shells, pearlash, sodic carbonate, and the carbonates generally, all yield carbonic anhydride when acted on by a strong acid.

Carbonic anhydride is also produced when carbon or carbonaceous substances are burnt in oxygen or in atmospheric air.

Properties.—Under the ordinary pressure of the atmosphere carbonic anhydride is a colourless, transparent gas, with a faintly acidulous smell and taste; but when generated in a confined space in strong vessels it becomes condensed to a liquid as transparent and colourless as water, which is a non-conductor of electricity. According to Regnault, it boils at $-78°$ ($-108°$ F.). At 0° (32° F.) it requires a pressure of 38·5 atmospheres to retain it in the liquid state (Faraday); it then has a specific gravity of 0·83, whilst at 86° (30° C.) the specific gravity is only 0·60. If these data be correct, the liquid expands by the application of heat four times more rapidly than air (Thilorier); but according to Andreeff (*Ann. Chem. Pharm.*, 1859, cx. 10) the expansion of the liquid, although greater than that of the gas, is not so great as Thilorier states. Andreeff found the density of the liquid 0·9471 at 0° C.; 0·8948 at 10°; 0·8635 at 15°; and 0·7831 at 25°, as compared with water at 4° (39°·2 F.). Liquefied carbonic anhydride does not mix freely with water, or with the fixed oils, and is only slightly soluble in carbonic bisulphide; but it is dissolved in all proportions by alcohol, ether, oil of turpentine, and naphtha. It dissolves iodine sparingly. When a stream of the liquefied body is allowed to escape into the air, it freezes into a snow-white solid (196): and if a tube containing liquid carbonic anhydride be plunged into a bath of the solid anhydride mixed with ether, and placed in the vacuum of the air-pump, the liquid in the tube will speedily be frozen into a clear, transparent, ice-like mass, which melts at $-57°$ ($-71°$ F.). The solidified anhydride is heavier than the liquid portion in which it is being formed. It is a curious fact that carbonic anhydride in the liquid state has been discovered in small cavities in rock crystal, topaz, sapphire, beryl, and tourmaline (Hartley, *Jour. Chem. Soc.*, 1876, I. 137 and II. 237).

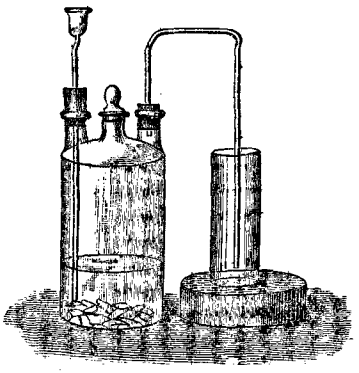
Gaseous carbonic anhydride is not inflammable, neither will it support the flame of burning bodies: the extinction of a taper is one of the means frequently resorted to for detecting its presence. Many other gases, however, have the same property; some additional test, therefore, becomes necessary. Such a test is afforded by its action upon lime-water, which, when agitated with the gas, is immediately rendered milky from the formation of chalk by the combination of the lime with the carbonic anhy-

dride; a few drops of any strong acid dissolve the chalk and restore the transparency of the liquid; an excess of carbonic acid even has the same effect.

Carbonic anhydride in its concentrated form is irrespirable, for by producing spasm of the glottis it is prevented from entering the lungs; when diluted with air, however, it may be breathed without even a suspicion of its presence. If the proportion exceed 3 or 4 per cent. of the air, it acts as a narcotic poison; and even in much smaller quantities its depressing effects are very injurious. It reduces both the frequency and power of the heart's action. The ill effects experienced in crowded and ill-ventilated rooms are partly due to the presence of this gas in undue quantity,* but partially also to the accumulation of volatile putrescible organic particles given off from the surface of the lungs and skin. It is the combination of these circumstances which renders attention to ventilation a matter of such high importance.

Gaseous carbonic anhydride is more than half as heavy again as atmospheric air; 1 litre at 0° C. and 760$^{mm.}$ weigh 1·977414 grams (Regnault), or 100 cubic inches of it at 60° F. and 30 inches Bar. weigh 47·307 grains; from its density it may easily be collected in dry vessels by displacement, in the manner represented in fig. 304, and may be poured from one vessel into another like water.

FIG. 304.



No definite hydrated carbonic acid is known; the anhydride, both in the form of gas and in its denser conditions of liquid and solid, being, as its name indicates, free from water; but it appears to be convertible into a true acid by solution in water, $CO_2 + OH_2$ yielding H_2CO_3. At 15° (59° F.) the gas is soluble in about its own bulk of water; and its solubility

* The maximum observed by Roscoe in his experiments on the atmosphere of dwelling houses, was 0·33 per cent., and this occurred in a crowded schoolroom.—(*Jour. Chem. Soc.*, 1857, x. 265) Angus Smith found on the average, from the examination of 339 specimens of the air in mines, as much as 0·78 per cent.; and in several extreme cases it exceeded 2·0 per cent. The quantity of oxygen in the air of these mines gave an average of 20 per cent., but in some cases it fell as low as 18·6.

increases if the temperature be diminished or the pressure increased;* on suddenly diminishing the pressure the gas escapes with brisk effervescence. Advantage is taken of this circumstance in the preparation of *soda-water*, as it is called. For this purpose the water, which may or may not contain soda or other substances in solution, is mechanically charged with a large quantity of carbonic acid, by the use of a condensing syringe, attached to a reservoir filled with the gas. The excess of the gas thus forced into the liquid occasions the agreeable briskness and pungency so much prized in this beverage.

A solution of carbonic acid in water changes the blue colour of tincture of litmus to a purple-red, which is quite distinct from the bright red produced by the stronger acids; this red colour disappears if the liquor be boiled for a few minutes, owing to the expulsion of the gas. The aqueous solution of the acid possesses solvent powers which, although in many instances extremely feeble, are yet far more extensive than those of pure water. By the continuous action of water charged with carbonic acid, even granite and the hardest rocks are disintegrated, few finely divided minerals being able to resist its gradual and long continued action. The proportion of gas dissolved in natural waters is in many instances very minute, but as few of them exist which are not to a greater or less extent impregnated with carbonic acid, either by absorption from the atmosphere or from the soil, the solution, insignificant as it may at first sight appear, is continually going on, and in the lapse of time it effects changes of great importance and extent.

The briskness of spring water, and the preference given to it as a beverage, is partly occasioned by the carbonic acid which it contains, although its usual coolness and the abundance of atmospheric air dissolved in it are still more important. It is the absence of these qualities, combined with the presence of traces of organic impurities, which renders the taste of boiled or distilled water flat and insipid (351).

(383) **Natural Sources of Carbonic Anhydride.**—Besides the processes for procuring the gas already described, there are many cases in which it is produced on a very large scale in nature.

1.—Respiration in man and animals is always attended with the formation of a large proportion of the gas. This fact may

* If the gas be simply passed through the water, the liquid seldom takes up more than two-thirds of its bulk.

be easily proved by blowing air from the lungs by means of a tube through lime-water, which will speedily become milky from the deposition of calcic carbonate. The proportion of carbonic anhydride in respired air varies from 3 to 4 per cent., being usually about $3\frac{1}{2}$ per cent.

2.—Carbonic acid is also formed abundantly in the process of fermentation, and is the cause of the briskness in bottled beer, champagne, and other fermenting liquors. Many accidents have occurred from persons incautiously descending into an empty fermenting-vat before the gas has had time to escape and mix with the air; it is usual to facilitate the escape of the dense gas by leaving the plug at the bottom of the vessel open for some hours.

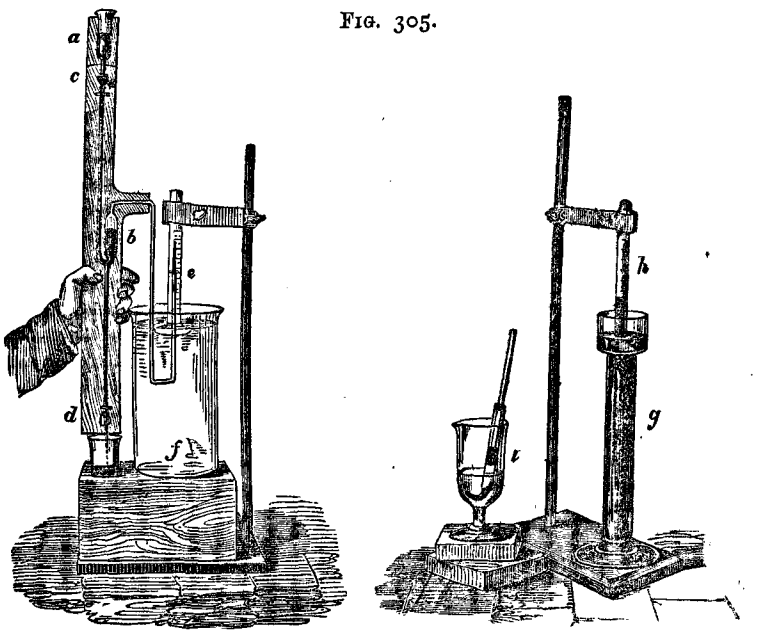
3.—In the operation of burning lime in the lime-kiln, the carbonic anhydride expelled from the limestone by the heat escapes in large volumes. Many a poor houseless wanderer, tempted by the warmth of the kiln, has lain down in the stream of air proceeding from it, and has slept to wake no more. By the operation of subterranean heat upon the limestone beneath the surface in certain volcanic districts, large volumes of carbonic anhydride are continually finding their way into the atmosphere; immense quantities are discharged from open craters or from fissures and cavities in the soil; the springs in such districts are also frequently highly charged with it, and the gas escapes with effervescence when they reach the surface. The springs of Seltzer, Pyrmont, and Marienbad, on the Continent, and of Tunbridge, in our own country, exhibit this phenomenon.

4.—The carbonic acid met with in spring water is in many instances derived from the gradual oxidation of the vegetable and other organic matter which it holds in solution, by the oxygen of the air which all waters naturally contain. The lake waters from the primitive districts, such as those in the northern parts of Scotland, leave scarcely any residue on evaporation except a little organic matter; they are very free from carbonic acid, and the volume of the oxygen which they hold in solution is somewhat more than one-half that of the nitrogen. If such waters be kept in closed vessels for a few weeks in a warm room, the oxygen gradually decreases, and its place is supplied by a corresponding volume of carbonic anhydride. The pure water of Loch Katrine, for example, when first collected did not yield more than 0·22 cub. centim. per litre, or 0·06 cubic inch, of carbonic anhydride per gallon; but the quantity of this gas which the same sample yielded after it had been kept in a close vessel for some weeks,

in a warm room, rose to 1·34 c.c. per litre, whilst the oxygen had diminished to a similar extent. Spring waters which rise in a sandy district, the surface of which is sparingly clothed with vegetation, and from which consequently they can take up but little organic matter, contain but small quantities, often mere traces, of carbonic acid; whilst the springs of highly cultivated districts, such as those which rest more or less directly upon the chalk, become charged with organic matter, which gradually undergoes oxidation in the soil, and the quantity of carbonic acid contained in such waters is always considerable, whilst the quantity of oxygen which they hold in solution is proportionately reduced.* The extent to which this change takes place in river

* The analysis of these gases, or of any mixture of air with carbonic anhydride, such, for example, as respired air, may be effected with sufficient accuracy for most purposes in the following manner:—Supposing that the gas had been collected over either water or mercury, it becomes necessary to transfer a portion of it from the jar in which it has been collected to the one in which it is to be analysed. A method of effecting this is shown in fig. 305. Upon the board,

FIG. 305.



a d, is fastened a pipette, designed for effecting this transfer; *a* is a cylindrical funnel of a capacity of about 30 cub. centim.; at *c* is a small stopcock of steel or glass, or a piece of vulcanized caoutchouc tubing compressed by a screw, which is simpler and less expensive; by either of these contrivances, the contents of the funnel can be admitted to a wide thermometer-tube, each portion of which

water is very remarkable. It is well exhibited in the case of the Thames.

On one occasion, some samples were taken from the river at low water at different points on the same day, in August, 1859; those collected above the

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must not be less than 30 centim. (12 inches) in length, and which is furnished at *d* with a second screw clamp: *b* is a bulb of the capacity of about 16 c.c. (1 cub. in.), from the upper part of which proceeds another piece of thermometer-tube, bent as shown in the figure, to allow of its introduction into the gas-jar; this bent portion may be connected to the bulb *b* with a flexible joint of caoutchouc tubing, by which the manipulation of the instrument is facilitated. To use the instrument, the funnel, *a*, is filled with mercury, the stopcocks are both opened, and as soon as the air has been displaced from the vertical portion of the fine tube, and mercury escapes through *d*, the lower stopcock is closed; the mercury quickly displaces the air from the rest of the tube, and from the bulb *b*, and as soon as it begins to flow out at the open extremity of the recurved portion, the stopcock, *c*, is closed. The instrument being now full of mercury is introduced into the jar, *e*, containing the gas to be transferred, and its open extremity is raised above the level of the water in the jar, *e*; the stopcock, *d*, is then opened, and whilst the mercury runs out into a vessel placed for its reception, the gas enters from *e*, and occupies the place of the mercury in the bulb, *b*. When a sufficient quantity has been admitted, the tube is depressed below the level of the water in the jar, *e*; the stopcock, *d*, is closed, and the pipette, which is sealed by the admission of a little water into the capillary tube, is withdrawn from the jar, *f*. The gas can now be transferred to the graduated tube, *h*, standing in the jar, of mercury, *g*; the bent limb of the pipette is introduced into the tube, *h*, which has been previously filled with mercury. Fresh mercury is poured into the funnel, *a*, of the pipette, and on opening the stopcock, *c*, the gas is expelled into the tube, *h*; the gas should not occupy more than two-thirds of the capacity of this tube.

The proportions of carbonic anhydride, of nitrogen, and of oxygen are now easily ascertained in the following manner:—The bulk of the gas in the tube, *h*, is to be carefully read off, care being taken to bring the mercury to the same level within and without the tube; the temperature and the pressure being observed as usual. Supposing that it has thus been ascertained that a bulk of gas of about 8 or 10 cub. centim. is to be subjected to the analysis, the operator, by means of a glass syringe, or a small glass pipette with a recurved tube, throws up 10 or 12 drops of a solution of potassic hydrate (density 1·4) into the tube. The glass syringe may be extemporaneously prepared from a strong tube which is softened in the flame of a lamp, drawn off and recurved at one end, as shown in the figure at *i*; this constitutes the body of the syringe, whilst the piston is easily formed of a piece of glass rod, provided with a plug of caoutchouc.

The operator then agitates the contents of the tube by rapidly thrusting down the tube into the mercury, and withdrawing it, taking care to keep the mouth below the surface of the mercury: this manœuvre is several times repeated in quick succession; the tube is again left at rest for a minute or two, and the absorption is noted by a second time reading off the volume of the gas at the proper level. The difference indicates the amount of carbonic anhydride.

In order to ascertain the proportion of oxygen in the remainder, the plan recommended by Liebig is the simplest:—A solution of 1 part of pyrogallic acid in 6 of water is prepared, and about 40 drops of the solution is, by

metropolis, being nearly free from contamination with sewage products, whilst those obtained lower down were extensively impregnated with them. The gases were expelled from each sample by boiling, within twenty-four hours from the time of its collection; the results obtained are given in the following table, in which they are contrasted with the proportions of each gas furnished by a similar experiment made with a sample of river water taken above Teddington Lock, where it was in a comparatively pure condition.

Temp. of river, 21°·1 C. 70° F.	Kingston.	Hammersmith.	Somerset House.	Greenwich.	Woolwich.	Erith.
Total quantity of gas in cubic in. per gallon .	14·67	Not determined.	17·49	19·77	17·50	20·64
Carbonic anhydride . .	8·42	Not determined.	12·56	15·42	13·40	15·80
Oxygen	2·07	1·16	0·43	0·07	0·07	0·52
Nitrogen	4·18	4·24	4·50	4·28	4·03	4·32
Proportion of Oxygen to Nitrogen . . .	1 : 2	1 : 3·7	1 : 10·5	1 : 60	1 : 52	1 : 8·1

From these experiments it will be seen that the water from Kingston (above Teddington) was thoroughly aërated, and contained oxygen in the proper proportion to the nitrogen, which when in solution is as 1 to 2. At Hammersmith, the effect of the organic impurities in abstracting the oxygen began to be evident. It was much more marked at Somerset House, whilst at Greenwich, where the condition of the river at low water was about at the worst, the oxygen had nearly disappeared. At Woolwich, it was nearly as bad, but by the time Erith was reached a great improvement was perceptible. Had the experiments been continued still lower down the river, the proportion of oxygen would doubtless have continued to increase, owing to the admixture of aërated sea-water and the absorption of oxygen due to the successive exposure of the water to the air in its onward flow.

5.—Carbonic anhydride is one of the principal constituents of what is termed *choke-damp* by miners, and often occasions much loss of life after the occurrence of an explosion of carburetted hydrogen, or *fire-damp*. It also accumulates frequently in the old workings of mines, and in pits or wells. Before descending into them, it is usual to lower a lighted candle in order to ascertain whether the light will burn; if it does so, it is generally considered safe to venture down. Instances, however, are on record in which a candle was found to burn in an atmosphere containing sufficient carbonic anhydride to cause death. When it is necessary to enter into an atmosphere considerably charged with this gas, Graham suggested as a precaution that the mouth

another clean pipette, injected into the tube, *h*, and the mixture briskly agitated as before; the solution of potash, if oxygen be present, becomes of an intense bistre-brown colour, and the oxygen is quickly and completely absorbed; the gas is measured a third time, and the residue is estimated as nitrogen; the difference between the second and third readings giving the volume of oxygen. A small quantity of carbonic oxide, amounting to between 2 and 3 per cent. of the volume of the oxygen is always formed in this operation.—(Crace Calvert; Boussingault.)

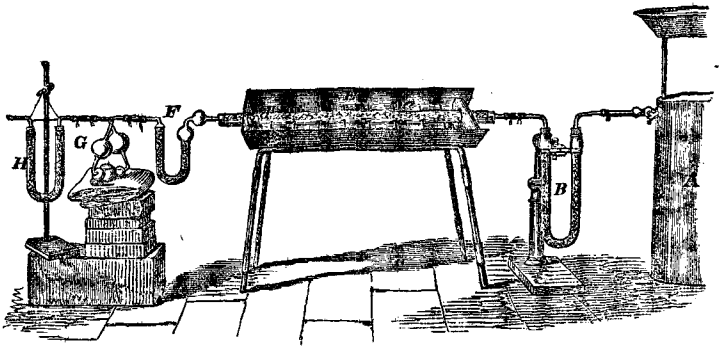
and nostrils be covered with a cloth containing a mixture of slaked lime and crystallized sodic sulphate. Such a mixture is porous enough, in a layer of $25^{mm.}$ or an inch thick, to allow the passage of sufficient air for respiration, whilst the moist lime completely absorbs the carbonic anhydride.

6.—There is also another mode in which carbonic anhydride is very largely formed, which, independently of its importance as a source of the gas, is interesting as throwing light upon its chemical nature. Whenever charcoal, or bodies which, like wood, coal, oil, or tallow, contain carbon, are burned either in oxygen or in air, carbonic anhydride is produced abundantly; if the gas, after the combustion has terminated, be agitated with lime-water, this liquid will be immediately rendered milky. According to Angus Smith, two candles in burning may be estimated to produce about as much carbonic anhydride as one man would emit by respiration during an equal interval of time, or about 1260 cubic inches (20·6 litres) per hour.

(384) **Synthesis of Carbonic Anhydride.**—Since a knowledge of the composition of carbonic anhydride is a fundamental datum for the analysis of organic compounds, the proportion in which oxygen combines with carbon to produce carbonic anhydride has been determined with the greatest care, by the combustion of weighed quantities of diamond, of graphite, and of charcoal, in a stream of dry oxygen.

The apparatus employed for this purpose is represented in fig. 306. A is a gas-holder filled with pure oxygen; B, a tube containing fragments of potassic hydrate, for removing all traces of moisture from the oxygen, as also any

FIG. 306.



carbonic anhydride that may be present: *c d* is a tube of hard glass traversing the sheet-iron furnace, E. At *c* is a platinum tray containing the weighed

portion of diamond or graphite; the front of the tube, *d*, is filled with cupric oxide, the object of which is to oxidize completely any trace of carbonic oxide which might be formed. The apparatus is filled with dry oxygen by partially opening the stop-cock of the gas-holder, A, and allowing a gentle current of the gas to pass through the whole apparatus, whilst the fore-part of the tube, *d*, is brought to a red heat by means of heated charcoal; the heat is then applied to the spot, *c*, where the carbon lies. The carbon burns and becomes converted into carbonic anhydride, which passes over the column of heated cupric oxide; F is a weighed tube, filled with calcic chloride, which, if water were present, would be found to increase in weight, but in which no deposit of moisture is formed if the experiment be properly conducted. The carbonic anhydride passes on, and is absorbed by a strong solution of potash contained in the bulbs of the Liebig's apparatus, shown at G. The excess of oxygen absorbs moisture as it passes through this liquid, but before it is allowed to escape into the air, it is rendered perfectly dry by causing it to pass through an additional tube, H, filled with fragments of potassic hydrate. The increase in weight acquired by the two tubes, G and H, furnishes the weight of the carbonic anhydride corresponding to the carbon consumed, whilst the amount of carbon burned is ascertained by weighing the platinum tray and its contents when the experiment is terminated.

By experiments conducted upon this principle, it has been determined that 12·0024 parts of carbon from diamond require exactly 32 parts of oxygen to convert it into carbonic anhydride (Dumas and Stas; *Ann. Chim. Phys.*, 1841, [3]. I. 5).

Diamond, graphite, and charcoal are thus shown to be chemically the same substance, although they differ entirely in properties; these three conditions being allotropic modifications of carbon, the differences in properties arising not from differences in their chemical nature, but in their molecular arrangement.

If a piece of pure carbon be burned in a jar of oxygen over mercury, it will be found after the combustion is over, and the gas has cooled to the original temperature of the oxygen, that the volume of the gas has undergone no permanent change: the carbonic anhydride formed occupies therefore the same volume as the oxygen it contains.

Carbon may again be extracted from carbonic anhydride. If a small piece of potassium, heated until it begins to burn in the air, be introduced by means of a platinum spoon into a jar of gaseous carbonic anhydride, the potassium will continue to burn with great brilliancy. Potassic oxide will be formed at the expense of the oxygen which the gas contains, whilst carbon will be liberated, as may be seen in the black particles suspended in the water into which the spoon is plunged after the combustion is complete. Thus carbonic anhydride is shown, both synthetically and analytically, to be a compound substance, consisting

of carbon and oxygen, and its composition may be represented as follows:

			By weight.	By vol.
Carbon	... C	= 12	or 27·27	... 1
Oxygen	... O_2	= 32	72·73	... 2
Carbonic anhydride	CO_2	= 44	100·00	... 2

Carbonic anhydride is not decomposed by such elevation of temperature as we can obtain in our furnaces, but if a succession of electric sparks be passed through the gas, or if it be submitted to the influence of the silent discharge, it is partially separated into carbonic oxide, and free oxygen. Sulphur, chlorine, and the halogens may be heated with the gas without decomposing it; but if mixed with hydrogen and exposed to a high temperature, water and carbonic oxide are formed, the decomposition which takes place being represented thus, $CO_2 + H_2 = CO + OH_2$. Carbon, and many of the metals, such as iron and zinc, also remove a portion of the oxygen from carbonic anhydride, and convert it into carbonic oxide (386).

Applications.—Sir G. Gurney has turned to an important practical account the property possessed by carbonic anhydride of extinguishing flame. Coal mines, at different times and from various causes, are liable to take fire, and from the vast mass of heated matter, the conflagration not unfrequently resists all the ordinary means of checking its ravages; many acres of subterranean fire are thus produced, and the workings are of necessity abandoned. Sir G. Gurney, in such cases, closes every opening into the mine but two, one for the entrance, the other for the escape of the gases, and then, by the agency of the steam jet, pours into the mine a current of impure carbonic anhydride and nitrogen, obtained by forcing a stream of air through a coke furnace into the mine, so as to fill the entire workings with the gas: he has thus on several occasions succeeded, at a very small expense, in extinguishing fires which have raged unsubdued for years.

A very remarkable case of this kind was mentioned in the *Times* for May 22, 1851:—The 'burning waste of Clackmannan,' situate about seven miles from Stirling, had been for 30 years on fire. It occurred in a seam of nine-foot coal, and extended over an area of 26 acres; yet the fire was successfully extinguished:—about 8,000,000 cubic feet, or 226,500 cub. metres, of gas were required to fill the mine, and a continuous stream of impure carbonic anhydride was kept up night and day for about three weeks. The difficulty lay not so much in putting out the fire, as in cooling down the ignited mass so that it should not again burst into flame on readmitting the air. In order to effect the necessary reduction of the temperature, water was blown in along with the

carbonic anhydride in the form of a fine spray or mist. Subsequently, cold air mixed with the spray was blown in, and in a month from the commencement of operations the fire was found to be completely extinguished.

(385) **Carbonates.**—Carbonic acid, until comparatively lately, was regarded as monobasic, but there is now no doubt that it ought to be considered a dibasic acid.

Although but a feeble acid, it forms a numerous and important class of salts called *carbonates*, which, with the exception of those of the alkali-metals, are insoluble in water; many of the insoluble carbonates, however, and particularly those of calcium, magnesium, barium, and strontium, may be dissolved to some extent by water charged with carbonic acid, and are deposited again in a crystalline form as the gas escapes slowly from the liquid. All the carbonates are dissolved with effervescence by dilute nitric acid, and even by acetic acid: the gas which comes off is colourless, renders lime-water turbid, and possesses the other characteristic properties of carbonic anhydride. The most delicate test of the presence of free carbonic acid is a solution of a basic salt of lead, such as the subnitrate or the subacetate; this is instantly rendered milky by the action of carbonic acid. The carbonates of the alkali-metals are also decomposed by acids with effervescence; their solutions give with calcic salts a white precipitate, which is immediately redissolved by an acid with evolution of carbonic anhydride. All the carbonates, with the exception of those of the alkali-metals and of barium, are decomposed by prolonged ignition, the salt being resolved into the anhydride and a metallic oxide. The carbonates have considerable tendency to combine with each other and form double salts, such as *dolomite*, which is a double carbonate of calcium and magnesium, $MgCa_2CO_3$ $\left[\begin{matrix}CO\\CO\end{matrix}(O_2Ca'')(O_2Mg)''\right]$. Many basic carbonates are also known: they are often hydrated compounds—such, for example, as *malachite*, $CuH_2O_2.CuCO_3$ $[CO(OCuOH)_2]$.

If M and M′ represent the atoms of any two different metallic monads, such as potassium and sodium, the general formulæ of the carbonates will be thus indicated:

Normal salt,	M_2CO_3	$[CO(OM)_2]$
Acid salt,	$MHCO_3$	$[CO(OH)(OM)]$
Double salt,	$MM'CO_3$	$[CO(OM)(OM')]$

The following table represents the composition of some of the most important carbonates:

Potassic carbonate	$K_2CO_3.OH_2$
Sodic carbonate	$Na_2CO_3.10OH_2$
Potassic hydric carbonate (bicarbonate)	$KHCO_3$
Sodic hydric carbonate (bicarbonate)	$NaHCO_3$
Trona (sodium sesquicarbonate)	$2Na_2CO_3.H_2CO_3.2OH_2$
Ammonic sesquicarbonate	$2[(H_4N)_2CO_3]CO_2$
Baric carbonate	$BaCO_3$
Calcic carbonate	$CaCO_3$
Magnesic carbonate	$MgCO_3$
Dolomite	$MgCa_2CO_3$
Baryto-calcite	$BaCa_2CO_3$
Malachite...	$CuCO_3.CuH_2O_2$
Blue carbonate of copper	$2CuCO_3.CuH_2OH_2$

§ III. CARBONIC OXIDE: CO=28.

(386) **CARBONIC OXIDE**, or *Carbon monoxide.—Observed Density* 0·9678; *Theoretic Density* 0·9688; *Mol. Vol.* [ ]; *Rel. wt.* 14.—It has already been stated that carbonic anhydride is wholly deprived of its oxygen when heated with potassium; but if some metal which has a less powerful attraction for oxygen, such as zinc or iron, be substituted for the potassium, the carbonic anhydride will only be partially deoxidized; the metal will deprive it of exactly half the oxygen which it contains, and a new gaseous body, termed *carbonic oxide*, will be produced. The bulk of this new gas is exactly equal to that of the carbonic anhydride that furnished it. Carbonic oxide, mixed with free hydrogen, is also obtained abundantly when steam is passed over charcoal heated to bright redness; $C+OH_2=CO+H_2$.

Preparation. 1.—Carbonic oxide may be prepared by mixing powdered chalk with an equal weight of iron or zinc filings, and exposing the mixture to a red heat in a gun-barrel. The chalk, when ignited, splits up into quick-lime, and carbonic anhydride, the latter of which is decomposed by the heated metal; this removes half the oxygen, forming oxide of iron or zinc, which remains in the retort mixed with the lime, whilst the carbonic oxide passes off in the gaseous state. In order to remove that portion of the carbonic anhydride which always escapes decomposition, the gas is washed with water containing slaked lime in suspension, and may now be collected over water, in which it is but slightly soluble. The chemical changes which take place when zinc is used may be represented in the following manner: $CaCO_3+Zn=CaO+ZnO+CO$.

2.—Carbonic oxide is often produced abundantly in the ordinary process of combustion in stoves and furnaces: this mode of

its formation is important, for it exercises a material influence upon the economy of combustion, inasmuch as all the carbonic oxide thus carried off unburnt represents so much fuel wasted; whilst in many metallurgic operations the carbonic oxide so produced plays a conspicuous part in the reduction of the ore to the metallic state, the oxides of iron, lead, copper, and many other metals, being reduced when heated with it, whilst carbonic anhydride is formed. It is owing to the production of carbonic oxide that anthracite can be employed in roasting the copper ores at Swansea, flame being essential to the due performance of the process. The formation of carbonic oxide in an open fire which is burning steadily without emitting smoke is often shown by the flickering blue flame seen playing over the glowing embers. In this case carbonic anhydride is first formed at the bottom of the grate, from the free access of air to this part of the burning fuel; but the carbonic anhydride as it traverses the red-hot coke enters into combination with an additional quantity of carbon, and the anhydride, losing half its oxygen, is converted into its own bulk of carbonic oxide: at the same time the carbon of the heated fuel which has entered into combination with this removed oxygen furnishes an equal volume of the same gas: the heated carbonic oxide takes fire as soon as it comes in contact with the air which passes over the upper surface of the fire. The reaction between the hot carbon and carbonic anhydride may be thus represented: $CO_2 + C = 2CO$.

Carbonic oxide may be prepared in the laboratory by passing a stream of carbonic anhydride over charcoal heated to redness in an iron tube.

3.—If a formate be treated with concentrated sulphuric acid, pure carbonic oxide is obtained:

$$\underset{\text{Sodic formate.}}{2NaCHO_2} + \underset{\text{Sulph. acid.}}{H_2SO_4} = \underset{\text{Carb. oxide.}}{2CO} + \underset{\text{Sodic sulphate.}}{Na_2SO_4} + \underset{\text{Water.}}{2OH_2}$$

$$\left[2\begin{Bmatrix} H \\ CO(ONa) \end{Bmatrix} + SO_2(OH)_2 = 2CO + SO_2(ONa)_2 + 2OH_2. \right]$$

4.—Carbonic oxide may also be prepared in several other ways. Half an ounce (15 grams) of the yellow prussiate of potash or potassic ferrocyanide, if heated in a retort with 4 or 5 ounces (140 grams) of concentrated sulphuric acid, yields more than a gallon (4 or 5 litres) of the pure gas (Fownes). Care is requisite in applying the heat, because when the temperature has risen to a certain point, the evolution of the gas takes place with tumultuous rapidity. The reaction is in this case of a complicated nature, but is expressed by the annexed symbols:

$$\underset{\text{Potassic ferrocyanide.}}{K_4FeC_6N_6} + \underset{\text{Water.}}{6OH_2} + \underset{\text{Sulphuric acid.}}{6H_2SO_4} =$$

$$\underset{\text{Carbonic oxide.}}{6CO} + \underset{\text{Potassic sulphate.}}{2K_2SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Ammonic sulphate.}}{3[(H_4N)_2SO_4]}.$$

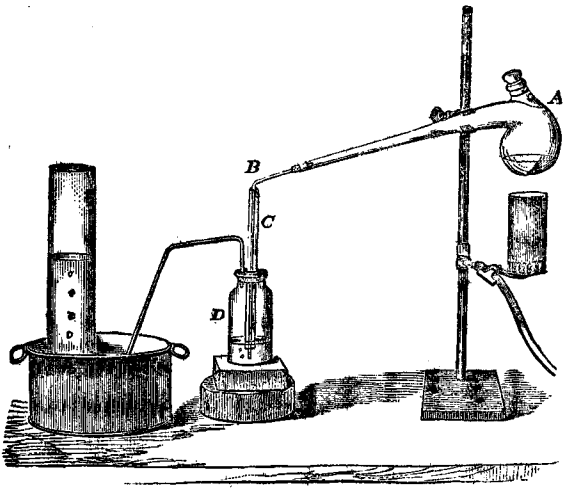
5.—Another method by which carbonic oxide may be obtained with facility consists in heating oxalic acid with 5 or 6 times its weight of sulphuric acid. The oxalic acid is thus deprived of the elements of water, and is resolved into a gaseous mixture consisting of equal volumes of carbonic anhydride and carbonic oxide: by allowing the mixed gases to pass through a vessel filled with a solution of potash, or with milk of lime, the carbonic anhydride is absorbed, and the purified carbonic oxide may be collected over water in the usual way. The decomposition may be thus represented:

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} - \underset{\text{Water.}}{OH_2} = \underset{\text{Carb. oxide.}}{CO} + \underset{\text{Carb. anhydride.}}{CO_2}.$$

$$\left[\begin{matrix}CO(OH)\\CO(OH)\end{matrix} - OH_2 = CO + CO_2.\right]$$

A convenient mode of washing the gas is shown at B, fig. 307: the bent tube is connected to the neck of the retort, A, and passes to the bottom of a wider tube, C, open both at top and bottom, which passes into the washing bottle, D: a moveable gas-tight joint is thus obtained, which can be mounted or dismounted in a moment.

Fig. 307.



If the gaseous mixture of carbonic anhydride and carbonic oxide, obtained by heating oxalic acid with concentrated sulphuric

acid, be passed through a tube filled with fragments of charcoal and maintained at a red heat, almost the whole of the carbonic anhydride present is converted into carbonic oxide, which may be purified as above described; by this modification of the process, three times as much carbonic oxide is obtained from the same weight of oxalic acid.

6.—Carbonic oxide may also readily be obtained by heating to low redness almost any of the normal oxalates, as potassic, sodic, or baric oxalate:

$$BaC_2O_4 = BaCO_3 + CO.$$

The gas prepared in this way is quite pure and free from carbonic anhydride.

Properties.—Carbonic oxide is a transparent colourless gas, with a faint oppressive odour. It is much lighter than carbonic anhydride, having a density of 0·9678. All attempts to liquefy it have as yet been unsuccessful. It is but very sparingly soluble in water, 100 volumes of this liquid dissolving only 3·287 volumes at 0° (32° F.), and 2·434 at 15° (59° F.) (Bunsen.) When respired, even although largely diluted with air, it acts as a direct poison, producing a peculiar sensation of oppression and tightness of the head. It does not support combustion, but burns with a beautiful pale blue light, combining with oxygen, and producing carbonic anhydride. A solution of cuprous chloride in hydrochloric acid, or of a cuprous salt dissolved in ammonia, gradually absorbs carbonic oxide if agitated with it. This solution is not decomposed by dilution, but if the liquid be boiled most of the gas is expelled unaltered. The compound with cuprous chloride crystallizes in fatty looking scales, consisting of $CO.Cu_2Cl_2.2OH_2$, which are quickly decomposed by exposure to the air. According to Böttinger (*Deut. chem. Ges. Ber.*, 1877, x. 1122), carbonic oxide is readily absorbed in large quantity by well-cooled dry hydrocyanic acid. Carbonic oxide unites with potassium if the metal be heated to about 80° (176° F.) in the gas, forming a compound of the formula $K_2C_2O_2$. This property is sometimes employed for separating carbonic oxide from other inflammable gases in the process of analysing mixtures of such gases.

Carbonic oxide unites with an equal volume of chlorine under the influence of sunlight, forming *carbonic oxydichloride* or *phosgene gas*, $CO + Cl_2 = COCl_2$.

Carbonic oxide has been supposed to form the radicle of a numerous series of compounds; it even enters directly into com-

bination with potassic hydrate when heated with it, converting it into potassic formate: $KHO + CO = KCHO_2$ [$OKH + CO = \left\{\begin{matrix} H \\ CO(OK) \end{matrix}\right\}$] Berthelot.

Composition.—The chemical composition of carbonic oxide may be ascertained in the following manner:—Introduce into the bent eudiometer (fig. 287) a certain quantity, say 20 measures, of carbonic oxide, then add 20 measures of pure oxygen; pass the electric spark with the precautions already described: the 40 measures of gas will become diminished to 30 measures. If a little solution of potassic hydrate be introduced, 20 measures of the residual gas will disappear, leaving 10 measures of unaltered oxygen: the 20 measures of gas absorbed are carbonic anhydride. Now carbonic anhydride contains its own bulk of oxygen, but the 20 measures of carbonic oxide have required only 10 measures, or half their bulk, of oxygen to convert them into the anhydride. Carbonic oxide therefore must have contained the other 10 measures of oxygen; in other words, half its bulk of oxygen. Therefore 2 vols. of carbonic oxide contains 1 vol. of oxygen, or 28 parts by weight of carbonic oxide contains 16 of oxygen; and its composition may be thus represented:

		By weight.	By volume.
Carbon	C = 12	or 42·86	?
Oxygen	O = 16	57·14	... 1
Carb. oxide	CO = 28	100·00	... 2

Carbonic oxide, and carbonic anhydride, widely as they differ in their properties, consist, it is evident, of the same elements; but the proportions of these differ in the two cases. Carbonic oxide is the compound of carbon that contains the smallest proportion of oxygen, the relative composition of the two bodies being:

		C.		O.		Carbon.		Oxygen.
Carbonic oxide ...	CO =	28 or 12	+	16	=	42·86	+	57·14
Carbonic anhydride	CO_2 =	44 or 12	+	32	=	27·27	+	72·73

In 100 parts.

CHAPTER IX.

NITROGEN—THE ATMOSPHERE.

§ I. NITROGEN: N = 14.

(387) **NITROGEN.**—*Theoretic Density* 0·9688; *Observed Density* 0·97137; *Atomic Volume* □; *Molecule in free state* NN □□; *Rel. wt.* 14; *Triad as in* $\dot{N}H_3$. *Pentad as in* NH_4Cl.—It has already been stated (345) that the larger proportion of the atmosphere consists of a gaseous body, which has been termed *nitrogen* (generator of nitre), because it is an essential constituent of nitre: sometimes the name of *azote* (from ἀ not, ζωή, life,) is given to it, because it is incapable of supporting life. This element was discovered by Rutherford in 1772.

Preparation.—The most convenient methods of obtaining nitrogen are based upon the removal of oxygen from atmospheric air.

1.—The simplest plan consists in placing a few fragments of phosphorus, previously dried by means of blotting-paper, on a porcelain dish floating upon the surface of the water in the pneumatic trough; the phosphorus is ignited by touching it with a hot wire, and a glass receiver filled with air is then inverted over it. The phosphorus burns at the expense of the oxygen in the confined air, and being partially converted into vapour by the heat which attends the combustion, is diffused through the gas, and thus quickly comes in contact and combines with every portion of oxygen: when cold, the nitrogen may be decanted into another jar and examined. A stick of phosphorus, if introduced into a jar of air which is standing over water, will slowly absorb the oxygen, even at ordinary temperatures, and in two or three days nearly pure nitrogen will be left amounting to about four-fifths of the original bulk of the air.

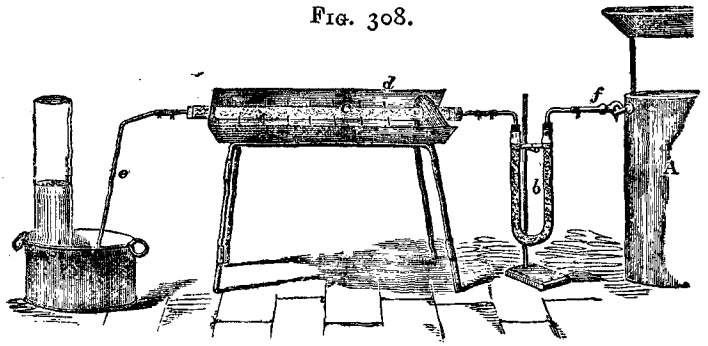
2.—The removal of oxygen from the air can also be effected slowly in various ways. Moistened iron filings may be used for this purpose, the metal gradually becoming oxidized, as is seen by the rusty appearance which it assumes. Many other metals in a moist state, such as lead shavings, produce a similar effect.

3.—Moistened sulphides of the alkaline metals likewise absorb oxygen from a confined portion of air very rapidly and completely.

4.—When larger quantities of nitrogen are required, metallic copper may be employed to remove the oxygen. The method to be adopted in this case is

exhibited in fig. 308 :—a long straight tube, *c*, of hard glass, which will resist a strong heat without fusion, is filled with metallic copper in a finely divided state; for this purpose the metal which has been reduced from the powdered

FIG. 308.



oxide by means of hydrogen gas is well adapted. The tube, *c*, which rests on a sheet-iron furnace, *d*, in which it can be surrounded by charcoal and raised to a red heat, has one of its extremities connected with a bent tube, *b*, filled with fragments of fused potassic hydrate, and to the other is adapted a bent tube, *e*, for delivering the gas into a jar over water or mercury; the air which supplies the nitrogen is driven from the gasholder, A, over the ignited copper in a stream which is easily regulated by the stopcock, *f*. The air first traverses the tube containing the potassic hydrate, which removes all traces of carbonic anhydride and water, and then passes over the ignited copper, which combines with and removed the oxygen, the nitrogen making its exit by the tube *e*.

5.—When the oxygen is removed from air by metallic copper as in the process just described, a large amount of copper is needed, and this is especially the case when copper turnings are employed; the coating of oxide formed soon retarding, and ultimately stopping, the action. This inconvenience is entirely obviated by mixing the air with ammonia previously to passing it over the copper, as suggested by Vernon Harcourt; the cupric oxide being reduced by the ammonia as fast as it is formed, with production of nitrogen and water: the reaction being

$$3(2N_2 + O) + 2NH_3 = 7N_2 + 3OH_2$$

(Air. Ammonia. Nitrogen. Water.)

Three inches of copper turnings in a glass tube heated by a Bunsen burner being quite sufficient to effect the decomposition; any excess of air showing itself by tarnishing the surface of the copper.

6 and 7.—Nitrogen may also be obtained by the action of chlorine on a solution of ammonia (392); and it is furnished in a state of purity by heating a solution of ammonic nitrite, or of ammonic chloride and potassic nitrite (p. 154).

8.—It may also be obtained by heating a mixture of potassic

dichromate and ammonic chloride in the proportions of 1 mol. of the former to 2 of the latter, the reaction being

$$K_2Cr_2O_7 + 2NH_4Cl = N_2 + Cr_2O_3 + 2KCl + 4OH_2.$$

Properties.—Nitrogen is a colourless, tasteless, and inodorous gas, which has hitherto resisted every effort to liquefy it.* It is somewhat lighter than atmospheric air; from Regnault's experiments, 1 litre at 0° C. and 760$^{mm.}$ pressure weighs 1·256167 grams, or 100 cubic inches at 60° F., Bar., 30 inches, weighs 30·052 grains. Water dissolves not more than a thirtieth of its bulk of this gas at ordinary temperatures, 100 volumes of water at 0° (32° F.) absorbing 2·035 vols of nitrogen, and 1·48 vols. at 15° (59° F.) (Bunsen). No two substances can offer a more striking contrast in chemical properties than oxygen and nitrogen: the former, one of the most energetic of the elements, the other, the most indifferent. It extinguishes a taper without taking fire itself: an animal immersed in the undiluted gas perishes quickly for want of oxygen, but it is not directly poisonous; indeed, it enters as a necessary component into the animal frame, and with every act of inspiration it finds admission into the lungs. One very important purpose that it fulfils in the atmosphere is the dilution of the oxygen, which is thus rendered less stimulating to the living system, and the rapidity of ordinary combustion is likewise thereby moderated. Nitrogen is one of the most extensively diffused forms of matter, as must be evident from the facts just stated; and notwithstanding its apparent indisposition to enter into combination, it forms a number of highly interesting and important compounds. For example, one of its compounds with oxygen, when united with water, forms nitric acid; and the potassic and sodic salts of this acid exist as natural productions. Nitrogen moreover is the characteristic ingredient in ammonia; and although it occurs in but small quantity in plants, it is never entirely absent from them. Nitrogen also constitutes an essential part of many of the most potent and valuable medicines as well as of some of the most dangerous poisons, such as quinine, morphine, prussic acid, and strychnine. It likewise enters largely into the composition of many animal tissues. Organic compounds which contain nitrogen are frequently termed *azotized* or *nitrogenous* substances.

* Quite recently oxygen, hydrogen, and nitrogen have all been reduced to the liquid state. Oxygen was first liquefied by Pictet at −140° (−220° F.) under a pressure of 320 atmospheres. Almost immediately afterwards Cailletet announced that he had succeeded in liquefying nitrogen and hydrogen.

§ II. COMPOSITION OF THE ATMOSPHERE.

(388) If a mixture be made of 4 measures of nitrogen and 1 measure of oxygen gas, a candle will burn in it as in atmospheric air; it may be breathed like air, and possesses the ordinary properties of the air. The atmosphere is, in short, a mechanical mixture of several gases, the great bulk of which consists of oxygen and nitrogen: these gases, notwithstanding their difference in density, are, owing to the principle of diffusion (67), uniformly mixed with each other. Chemical operations are continually occurring upon the earth's surface, which remove oxygen and add a variety of other gases, amongst which carbonic anhydride is the most abundant. Yet so wonderfully adjusted is the balance of chemical actions over the face of the earth, that no perceptible change in the composition of the atmosphere has been observed since accurate experiments on the subject have been practised.

Air which has been freed from carbonic anhydride and aqueous vapour consists, according to the numerous and careful analyses of Dumas and Boussingault (*Ann. Chim. Phys.* 1841, [3], iii. 257), on an average of 20·81 of oxygen by measure, and 79·19 of nitrogen in 100·00 vols.; or by weight of 23·01 of oxygen, and 76·99 of nitrogen. These experiments were performed by allowing the air to stream slowly over a weighed quantity of heated copper, by which the oxygen was absorbed (fig. 308), whilst the nitrogen was received into an exhausted flask, which was weighed before the experiment was commenced and after its termination; the quantity of oxygen was found by the gain in weight experienced by the tube containing the copper. The results obtained by Regnault, Brunner, Verver, Bunsen, and others, by different methods of analysis, do not vary more than $\frac{1}{500}$ from the quantity of oxygen just mentioned. Trifling temporary variations no doubt occur from local causes; but the air brought by Gay-Lussac from an elevation of four miles above the surface of the earth, that collected on the summit of the Alps, and that examined both in town and country in various parts of the globe, presents no sensible difference from the mean above given.

A portion of air collected by Mr. Welsh, in August, 1852, at an elevation of 5486 metres, or 18,000 feet, in one of the balloon ascents undertaken by him and Mr. Green under the direction of the Kew Committee of the British Association, contained 20·88 per cent. of oxygen by volume, whilst air collected at the surface at the same time contained 20·92. The air was collected in tubes of about 6 cub. in., or 100 cub. centim. in capacity, fitted with accurate stopcocks. They were exhausted previously to the ascent, and were filled with the air for examination by opening the stopcocks, which were again closed as

soon as the charge had entered. In the extensive series of experiments of Regnault (*Ann. Chim. Phys.*, 1852 [3], xxxvi. 385), air was collected at different points of the earth's surface in glass tubes, drawn out to an open capillary extremity at either end, fig. 309. When a specimen of air was to be collected,

FIG. 309.

one of these tubes was attached by a flexible tube to a small pair of bellows, and by working the bellows a few times, the tube was filled with air of the locality. The capillary tubes were then drawn off and sealed, as at *a* and *b*, by momentary contact with the flame of a spirit-lamp, and the closed ends were protected from injury during the journey by small caps of glass tube fitted with corks. The analyses of the air thus obtained were executed by means of hydrogen, in a eudiometer of Regnault's contrivance. The same apparatus was used by the late Professor Miller in the analyses of the air collected by Mr. Welsh. Frankland found 20·96 of oxygen in air collected by himself from the summit of Mont Blanc, whilst Bunsen, as the mean of seventy-eight analyses of air, found 20·924 of oxygen.

The following are results of some of the most trustworthy experiments upon the weight of air, calculating from the experiments

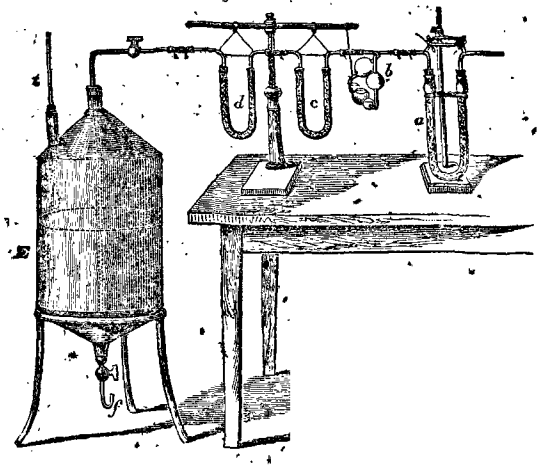
		Grains at 60° F. 30 in. Bar.	Grammes at 0° C. 760 mm.
of Dumas and Boussingault .	100 cubic inches.	31·118	1·299500
of Biot and Arago		31·117	1·299100
of Prout		31·0117	1·292618
of Regnault		31·025	1·293187

The second result is probably the most accurate, for it exactly corresponds with the density deduced from that of a mixture of oxygen and nitrogen in the proportions in which they occur in the atmosphere. A cubic metre of air, according to this result, at 0° C. and 760$^{mm.}$ pressure, weighs 1·2991 kilograms, or a cubic foot under a pressure of 30 inches Bar., weighs 538·569 grains at 60°. The weight of a given volume of air at 60° F., under a pressure of 30 inches Bar., is therefore only $\frac{1}{816}$ of that of an equal bulk of water at the same temperature, or $\frac{1}{773}$ at 0° C., and 760$^{mm.}$ barometric pressure. Owing to the greater solubility of oxygen than of nitrogen, rain water and melted snow always contain a larger proportion of oxygen than the air itself, amounting to about 34 per cent. of the air dissolved, or nearly one volume of oxygen to two volumes of nitrogen. This is a circumstance of great importance to aquatic animals, and one which could occur only in consequence of the air being a mechanical mixture and not a chemical compound of the two gases (64).

In addition to oxygen and nitrogen, the atmosphere contains a certain proportion of carbonic anhydride, a variable but minute trace of ammonia, traces of nitric acid, and of some compound of carbon and hydrogen, and frequently in towns a perceptible amount either of sulphurous anhydride or of sulphuretted hydrogen. Aqueous vapour is, of course, also present at all times, although its amount is liable to extensive fluctuations.

(389) **Estimation of Aqueous Vapour.**—The amount of aqueous vapour at any spot may be ascertained by means of the hydrometer (194), or it may be determined by direct experiment in the following manner. A bent tube, *a*, fig. 310, filled with pumice-stone moistened with sulphuric acid, is connected with a vessel, E, of known capacity; suppose it be capable of containing 80 litres, or about 18 gallons of water. This vessel having been filled with water, is allowed to empty itself slowly by opening a stopcock, *f*, which terminates in a tube bent upwards to prevent the entrance of air at the bottom; a known volume of air is thus drawn through the tube *a*, which retains all the moisture. If the weight of this tube be determined before commencing the experiment, and a second time after it is completed, the increase in weight will indicate the amount of moisture in the bulk of air operated upon. The temperature is ascertained by means of the thermometer, *t*, and the atmospheric pressure is obtained by an observation of the barometer at the time. The flow of water from the aspirator is rendered uniform during the whole course of the experiment, by making the tube which conveys the air sufficiently long to reach nearly to the bottom of the vessel, as shown by the dotted line which passes down from the central opening at the top.

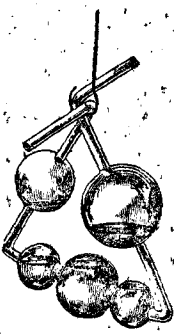
FIG. 310.



(390) **Estimation of Carbonic Anhydride.**—The quantity of carbonic anhydride in the air may be determined in the course

of the same experiment. If the bulbs at *b* be filled with a strong solution of potassic hydrate (density 1·25), and the tube *c* with fragments of fused potash, the gain in weight experienced by the tubes *b* and *c* will indicate the quantity of carbonic anhydride which has been absorbed in the operation; the bent tube, *d*, is filled with pumice-stone moistened with sulphuric acid; it is not weighed, but is merely interposed as a measure of precaution between the aspirator E, and the tube *c*, to prevent any accidental trace of moisture from passing backwards into *c*. The bulbs seen at *b* are to be filled with solution of potassic hydrate to the extent shown in the enlarged drawing, fig. 311. This form of apparatus was contrived by Liebig. It is in continual requisition in the laboratory for the purpose of absorbing gases which are passed through it; by placing it a little on one side, the gas is made to bubble up successively through each of the three lower bulbs, besides being brought thoroughly into contact with the liquid in the narrow portions of the tubes which connect the different bulbs together. This simple contrivance has added greatly to precision in experiments of this kind.

FIG. 311.



Pettenkofer estimates the quantity of carbonic anhydride in air by agitating a given volume of the air for trial with a measured amount of lime-water or baryta-water of known strength. The lime- or baryta-water used for this purpose is graduated by the alkalimetric method, by means of a standard solution of oxalic acid. The carbonic anhydride neutralizes and precipitates a certain quantity of lime or baryta in the form of carbonate, and the quantity of lime or baryta which remains in the solution after the experiment is again determined by the solution of oxalic acid. The difference in the quantity of lime or baryta, before and after its action upon the air enables the operator to calculate the proportion of carbonic anhydride with great accuracy.

The proportion of carbonic anhydride in the atmosphere varies from 3 to 6 parts in 10,000 of air (Truchot, *Compt. Rend.*, 1873, lxxvii. 675; Schultze, *Jour. Chem. Soc.*, 1872, xxv. 668; Henneberg, *ibid.*, 1873, xxvi. 595). De Saussure found that, within these limits, its amount is lessened after rain, owing to the solvent action of the descending shower carrying a portion of the gas with it to the earth. It increases during a frost, and diminishes when a thaw sets in. It is more abundant in summer than in winter. During the night it increases, and diminishes again after sunrise. It is less in amount over large bodies of water, than over large tracts of land. The proportion of carbonic anhydride is less liable to vary on elevated mountains, where it

is generally more abundant, than in the plains. It is also more abundant in densely populated districts, than in the open country. In inhabited dwellings, and in rooms for public assemblies, in metal and coal mines, &c., the proportion of carbonic anhydride may, however, greatly exceed the normal amount. Angus Smith, from an examination of the air from a great number of mines, found the mean amount of carbonic anhydride to be 0·785 per cent. The quantity of ammonia and nitric acid in the atmosphere is materially diminished after long continued and heavy rains. Occasionally, from local and accidental circumstances, other gases and vapours are also met with. The air of towns contains in addition certain organic impurities in suspension. Angus Smith has attempted to estimate their amount by measuring the quantity of a very dilute solution of potassic permanganate of known strength which a given bulk of air will decolorize. (*Jour. Chem. Soc.*, xi. 217, and *Report on Air in Mines*, 1864, p. 53; *Reports of the Inspector under the Alkali Act of* 1863.)

The average composition of the atmosphere in the climate of England may be approximately stated as follows, in 100 parts by volume:

Average Composition of the Atmosphere.

	Oxygen	20·61
	Nitrogen	77·95
	Carbonic anhydride	·04
	Aqueous vapour	1·40
	Nitric acid	traces
	Ammonia	
	Carburetted hydrogen	
and in towns	Sulphuretted hydrogen	traces
	Sulphurous anhydride	

If air which has been scrupulously freed from carbonic anhydride be passed over a column of pure ignited cupric oxide, traces of carbonic anhydride are always obtained, owing to the oxidation of some combustible compound of carbon. In the junctions of the apparatus employed for this experiment the use of cork and caoutchouc must be avoided (Karsten), or otherwise carbonic anhydride might be derived from them.

CHAPTER X.

COMPOUNDS OF NITROGEN.

§ I.—COMPOUNDS OF NITROGEN WITH HYDROGEN AND CHLORINE.

(391) **AMMONIA**, *Volatile Alkali, or Spirit of Hartshorn*, $NH_3 = 17$. *Melting-pt.* -75° (-103° F.); *Boiling-pt.* $-38^\circ{\cdot}5$ ($-37{\cdot}3^\circ$ F.); *Theoretic Density* 0·5882; *Observed Density* 0·59; *Mol. Vol.* [ ]; *Rel. wt.* 8·5.—This important compound has received the name of ammonia, from the circumstance of its having been obtained from a salt termed sal ammoniac, first procured near the temple of Jupiter Ammon, in Libya; hence its name. When a mixture of nitrogen and hydrogen is submitted to the silent discharge, a portion of the gases combine and form ammonia, but according to Berthelot (*Bull. Soc. Chim.*, 1876 [2], xxvi. 101), the amount of this never exceeds the limit of 3 per cent. of the total volume of gas: on the other hand, when ammonia is acted on in a similar manner, it continues to be decomposed until the same proportion remains unattacked. Ammonia is also formed during the spontaneous decomposition of moist animal matters, which contain both hydrogen and nitrogen, and indeed in almost every process of oxidation by air in the presence of moisture. The hydrogen, at the moment of its liberation from the water by deoxidation, appears to enter into combination with the nitrogen of the atmosphere, which, to a small extent, is held in solution, and thus ammonia is formed. If a current of nitric oxide be passed over a mixture of potassic hydrate and slaked lime, nitrates of potassium and calcium are formed, whilst ammonia is generated. Moistened iron filings, if exposed to the air, become rusty, and the oxidized compound retains a small quantity of ammonia.

The deoxidation of dilute nitric acid by the metals also frequently gives rise to the formation of ammonia; two atoms of oxygen changing places with four of hydrogen:

$$\underset{\text{Nitric Acid.}}{NO_2.OH} + 4H_2 = \underset{\text{Ammonic Hydrate.}}{NH_4.OH} + \underset{\text{Water.}}{2OH_2}.$$

$$[NO_2(OH) + 4H_2 = NH_4(OH) + 2OH_2.]$$

Tin, zinc, and iron exhibit this effect in a marked degree (400). This reaction has been used as a means of estimating the

quantity of nitric acid in solutions; for by dissolving zinc very slowly in dilute hydrochloric acid, and adding the nitric solution in small quantities at a time, the whole of the nitric acid is converted into ammonia. (Nesbit, *Jour. Chem. Soc.*, 1849, i. 281.) Harcourt has improved upon this method (*Jour. Chem. Soc.*, 1862, xv. 381); he distils the concentrated liquid with potassic hydrate and a mixture of granulated zinc and iron turnings, and receives the distillate containing the ammonia into a known weight of a standard solution of sulphuric acid. A still more delicate method is that of Schultze (*Chem. Centr.*, 1861) and of Chapman (*Jour. Chem. Soc.*, 1868, xxi. 173) of treating the solution containing the nitrate with metallic aluminium and a solution of pure caustic soda.

When a mixture of 2 volumes of nitric oxide and 5 of hydrogen is passed over spongy platinum or platinized asbestos gently heated, water and ammonia are produced. Hadow has also observed the formation of ammonia when nitrous acid and peroxide of nitrogen are reduced by passing them through a solution of hydric potassic sulphide, KHS, or of ferrous acetate.

Ammonia exists in minute quantity in the atmosphere.

According to the elaborate researches of Ville, which appear to have been conducted with every precaution to insure accuracy, one million kilograms of air contained on the average, in the year 1849, 24·7 grams of ammonia, and in 1850, 21·1 grams. This amounts to about one volume of ammonia in twenty-eight million volumes of air, or 0·35 c. c. of the gas in 1 cubic metre of air. Other experimenters make the quantity considerably higher. The proportion of ammonia contained in rain water is liable to considerable variation: in 1,000,000 parts of rain water collected in Paris during the last five months of 1851, Barral found 3·49 parts: Boussingault, at Liebfraunberg, in 1852, found only 0·744 parts; and Lawes and Gilbert, at Rothamsted, in 1853 and 1854, found the average amount from March to August to be 1·142, from September to February 0·927 parts; the average of the last two determinations would give about 1 grain of ammonia in 14 gallons of rain water, or about 1 gram of ammonia in a cubic metre of rain water. Boussingault has corroborated Barral's results by experiments upon the rain collected in Paris; indeed it is not surprising that in a populous city, crowded with animal life, and with the exuviæ of animals, the proportion of ammonia in its atmosphere should be much higher than in the surrounding districts. It appears, also, that a larger quantity of ammonia is always contained in the water that is collected at the commencement of a shower than at the end of it, and more after a drought than after a period of rainy weather. In the water of dews and fogs, also, the amount of ammonia was found to be much higher than in rain water. The proportion of ammonia in water derived from the atmosphere is, in short, greater, the smaller the fall, a circumstance which is easily accounted for by the high solubility of the gas in water. The atmospheric supply of ammonia is intimately connected with the assimilation of nitrogen by plants.

Ammonia is also found in clayey, and in peaty soils, both of

which absorb it freely. When nitrogenous matters are heated with the hydrated alkalies, they are decomposed, and the whole of the nitrogen, unless present in the form of a nitrate or a cyanide, is disengaged as ammonia; upon this fact is based the usual method of determining the amount of nitrogen in organic compounds. For the purposes of manufacture, however, ammonia is always procured by the distillation, in closed vessels, of organic matters containing nitrogen. During the distillation of bones, and of animal refuse generally, ammonia is formed in considerable quantity, and condenses along with the empyreumatic products of the operation. Almost the whole of the ammonia used in the arts is obtained, however, from bye products in the distillation of coal for the manufacture of gas. Amongst these products is the ammoniacal liquor of the gas-works, consisting of an aqueous solution of ammonic carbonate and sulphide; this liquor, when neutralized with sulphuric or hydrochloric acid, furnishes ammonic sulphate or chloride (the sulphate or muriate of ammonia of commerce).

Preparation.—If equal weights of quick-lime with either the sulphate or muriate of ammonia be separately powdered and intimately mixed, the powder, on being transferred to a retort and gently heated, gives off abundance of pure ammonia, as a transparent, colourless gas, of the peculiar, pungent odour of smelling salts: 1 ounce of ammonic chloride, if fully decomposed, would yield about 750 cubic in. or 30 grams; about 12½ litres of the gas. The lime combines with the acid and sets the ammonia at liberty, calcic chloride and water being formed; the result when ammonic chloride is used being as follows:

$$\underset{\text{Lime.}}{CaO} + \underset{\text{Ammonic chloride.}}{2NH_3HCl} = \underset{\text{Calcic chloride.}}{CaCl_2} + \underset{\text{Water.}}{OH_2} + \underset{\text{Ammonia.}}{2NH_3}.$$

$$[CaO + 2NH_4Cl = CaCl_2 + OH_2 + 2NH_3.]$$

Ammonia as thus prepared from commercial ammonic salts invariably contains a minute quantity of organic bases; absolutely pure ammonia, however, may be obtained by digesting a solution of potassic nitrite and potassic hydrate, with granulated zinc free from carbon and iron wire which has been ignited in contact with the air and subsequently reduced in a current of hydrogen; the solution when poured off from the metal and cautiously distilled yields ammonia quite free from any organic impurity. (Stas, *Zeits. anal. Chem.*, 1867, vi. 423.)

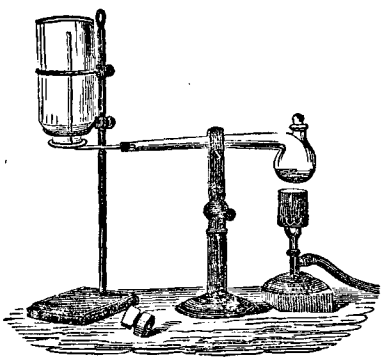
Properties.—Ammonia possesses a very pungent odour, inducing a copious flow of tears; it has an acrid taste, and, when

breathed in a concentrated form, is fatal to life, from its irritating effects on the lungs. In a more diluted form, it is a highly valuable stimulant.

Ammonia does not support the flame of burning bodies, but is feebly combustible; a jet of the gas directed across the stream of hot air issuing from a lighted argand lamp, burns with a very pale greenish-yellow flame, and it can be kindled readily in an atmosphere of oxygen. If the gas be mingled with an equal bulk of oxygen, the mixture may be detonated by means of the electric spark; water, nitrogen, and traces of nitric acid being formed. If a mixture of ammonia with air or oxygen be passed over spongy platinum, water and nitric acid are amongst the products. If a stream of ozonized air be passed into a bottle containing a small quantity of a concentrated solution of ammonia, dense white fumes of ammonic nitrite are formed, owing to the oxidation of the ammonia by the ozone.

Ammonia is extremely soluble both in alcohol and in water, which renders it necessary to collect it either over mercury, or by displacement in the manner shown in fig. 312. The latter mode of collecting it may easily be effected, as the gas has little more than half the density of atmospheric air, its density being only 0·59. Ammonia has a powerfully alkaline reaction, and turns turmeric paper brown. When collected by displacement, the gas must be allowed to pass into the bottle until a piece of dry turmeric paper held to the mouth of the bottle is immediately turned brown; the tube is then withdrawn, and the stopper is inserted after having been slightly greased. Ammonia is much less soluble in solutions of potassic or sodic hydrate than in pure water, whilst a solution of potassium nitrate absorbs more ammonia than water does.

Fig. 312.



Ammonia neutralizes the most powerful acids, and forms a very important class of salts. Any volatile or gaseous acid brought into an atmosphere containing ammonia, produces a white cloud, owing to the formation of a solid salt. This property is often employed to detect small quantities of ammonia: slaked lime or potassic hydrate is added to the solution suspected

to contain ammonia, and the mixture is then gently warmed in a tube; if a rod moistened with hydrochloric acid diluted with half its bulk of water be now introduced into the upper part of the tube or vessel, white fumes will make their appearance if ammonia be present, even when the quantity is too small to be distinguished by the smell. When ammoniacal gas is required in a state free from moisture, it must be dried by passing it over quick-lime or fused potassic hydrate, and not over calcic chloride; for the latter, like many other saline compounds, absorbs ammonia and forms with it a definite compound.

Ammoniacal gas may be liquefied by exposure to a cold of $-50°$ ($-58°$ F.), or still more readily by generating it under pressure. The easiest method is the following:—

Argentic chloride in powder is exposed to a current of dry ammoniacal gas; the ammonia is rapidly absorbed, and the chloride increases in weight more than one-third. This substance is placed in one limb of a strong tube bent to an obtuse angle, and then hermetically sealed; on applying heat to the chloride, and cooling the other end of the tube with a freezing mixture, the ammonia is condensed as a colourless liquid, which boils at $-38°{\cdot}5$ ($-37°{\cdot}3$ F.) (Regnault), exerts a pressure of 6·9 atmospheres at $15°{\cdot}5$ (60° F.), and has a specific gravity of 0·6364 at 0° (32° F.) (Andréef, *Ann. Chem. Pharm.*, 1859, cx. 1), or 0·6234 according to Jolly (*ibid.*, 1861, cxvii. 181). By a cold of $-75°$ ($-103°$ F.), it is frozen to a white, translucent, crystalline solid, which is denser than the liquid. The argentic chloride reabsorbs the liquefied ammonia at ordinary temperatures, and slowly reproduces the original compound. Advantage has been taken of the cold produced by the evaporation of liquefied ammonia to prepare ice on a large scale. The form of apparatus originally employed by Carré (Pt. I., p 387, *note*) has since been greatly improved by Rice Reece. Liquefied ammonia possesses the peculiar property of dissolving the alkaline metals, lithium, potassium, and sodium, forming beautiful blue solutions, from which the metal is deposited unchanged on evaporation of the ammonia.

Composition.—The composition of ammonia may be ascertained as follows:—If the dry gas be subjected to a succession of electric sparks from a Ruhmkorff's coil, or if it be passed slowly through a porcelain tube containing iron or copper turnings, heated to bright redness, the gas is decomposed, and at the same time becomes dilated to double its original volume: 4 volumes of ammonia become 8; and the gas produced may be shown by detonation with oxygen in a eudiometer, to consist of a mixture of 2 volumes of nitrogen with 6 of hydrogen. If, after adding 8 measures of this mixture to 4 of oxygen, so as to make 12 measures in the whole, the electric spark be passed, 3 measures will be left, owing to the formation of steam and its subsequent condensation. Since in the formation of water 2 measures of hydrogen combine with 1 measure of oxygen; one-third of the volume of gas which has disappeared, or 3 measures, will be

oxygen, and two-thirds, or 6 measures, will be hydrogen. On agitating the residual gas with a solution of potassic hydrate, no change of bulk will occur, consequently no carbonic anhydride can have been formed; but on the addition of pyrogallic acid (*note* 383) to the gas whilst still in contact with the alkaline liquid, the excess of oxygen will be absorbed. This will amount to 1 measure, whilst 2 measures of nitrogen remain unacted upon; 2 measures of nitrogen must therefore have been present in the ammonia in combination with 6 of hydrogen which have become condensed as water; consequently, since the ammonia doubles its volume when decomposed by heat, the 4 volumes of ammonia must have been formed by 6 volumes of hydrogen and 2 of nitrogen, condensed into half their bulk. The composition of ammonia may therefore be thus represented:

		By weight.	By vol.
Hydrogen	H_3 =	3 or 17·65	... 3
Nitrogen	N =	14 82·35	... 1
Ammonia	NH_3	17 100·00	... 2

Other striking proofs of the composition of ammonia are afforded by the action of heat upon some of its salts; for instance, when ammonic nitrate, $NH_4.NO_3$, is heated, it is decomposed into water and nitrous oxide, $2OH_2 + N_2O$; the 4 atoms of hydrogen in the ammonium combining with 2 of the oxygen to form water, whilst the nitrogen of the ammonium as well as that of the nitric acid uniting with the remaining atom of oxygen produces nitrous oxide. If a solution of ammonic nitrite be heated, the salt is decomposed into water and nitrogen; the result may be thus represented, $NH_4.NO_2 = 2OH_2 + N_2$: the hydrogen of the ammonium is in this case exactly sufficient to combine with all the oxygen, forming water: this is an excellent mode of procuring pure nitrogen. When nitrogen is to be prepared in this way, the most convenient method of obtaining the potassic nitrite for this purpose is to saturate a solution of caustic potash of density 1·38, with nitrous acid disengaged by acting upon starch with nitric acid of density 1·25. This solution, if it be left slightly alkaline, may be preserved without alteration, and when wanted for the preparation of nitrogen, may be mixed with three times its bulk of a saturated solution of sal ammoniac, and gently heated in a small retort: nitrogen is evolved abundantly, and with great regularity (Corenwinder).

Nitrogen may also be prepared by heating an intimate mix-

ture of finely powdered ammonic chloride and potassic dichromate; in this case the reaction is thus represented:

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + OH_2 + 2KCl + N_2.$$

Chlorine also decomposes ammonia at ordinary temperatures, and liberates nitrogen gas. Under certain circumstances it produces the detonating compound known as chloride of nitrogen (396).

(392) **Solution of Ammonia.**—A solution of ammonia in water is a reagent continually required in the laboratory. Ammoniacal gas is rapidly absorbed by water with considerable development of heat; at a temperature of 0° (32° F.), Carius (*Ann. Chem. Pharm.*, 1856, xcix. 129) found that water takes up about 1050 times its volume of the gas; at 15° (59° F.) 727 times its volume; and at 25° (77° F.) 586 times its volume: according to Roscoe and Dittmar (*Jour. Chem. Soc.*, 1859, xii. 147), one gram of water when saturated with ammonia at 16° (60°·8 F.) under a pressure of 760 millim. absorbs 0·582 of its weight of the gas, increasing in bulk nearly one-half, and becoming specifically lighter; at 0° (32° F.) it absorbs 0·875 of its weight. The following table indicates the strength of solutions of pure ammonia of different specific gravities:

Strength of Solutions of Ammonia at 14° (57°·2 *F.*) (*Carius*).*

Ammonia in 100 parts by weight.	Density.	Ammonia in 100 parts by weight.	Density.	Ammonia in 100 parts by weight.	Density.	Ammonia in 100 parts by weight.	Density.
36	0·8844	27	0·9052	18	0·9314	9	0·9631
35	0·8864	26	0·9078	17	0·9347	8	0·9670
34	0·8885	25	0·9106	16	0·9380	7	0·9709
33	0·8907	24	0·9133	15	0·9414	6	0·9749
32	0·8929	23	0·9162	14	0·9449	5	0·9790
31	0·8953	22	0·9191	13	0·9484	4	0·9831
30	0·8976	21	0·9221	12	0·9520	3	0·9873
29	0·9001	20	0·9251	11	0·9556	2	0·9915
28	0·9026	19	0·9283	10	0·9593	1	0·9959

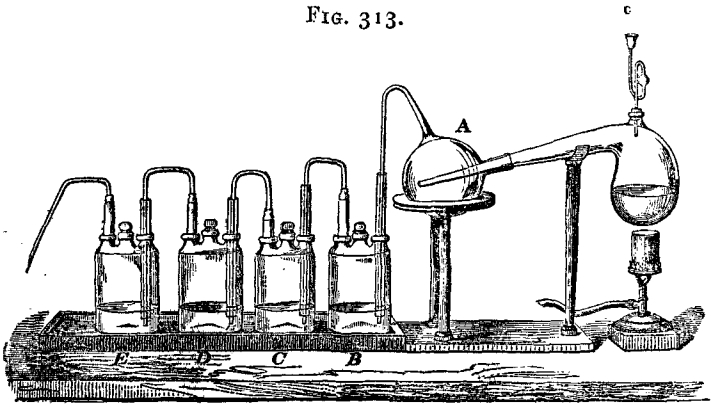
Solution of ammonia is colourless and intensely alkaline; it has an acrid, caustic taste, and blisters the skin if applied to it in a concentrated form; it freezes at about −40°, yielding a gela-

* An elaborate table of the strength of solutions of ammonia at 12° (53°·6 F.), by Wachsmuth, is given in *Jour. Chem. Soc*, 1876, ii. 477 (from *Arch. Pharm.* [3], vi. 510), in which the percentages are somewhat lower than those given by Carius. The author found that water at 0° (32° F.) dissolved 1193 times its volume of ammonia, increasing in volume from 100 to 203. The density of the solution was 0·866.

tinous mass of needles, destitute of odour. Simple exposure of the solution to the air at ordinary temperatures is attended with an escape of the gas, which occasions the pungent smell of the liquid. The ammonia is expelled rapidly by heat, with the appearance of ebullition, thereby furnishing a ready extempore method of procuring the gas. On heating the liquid for a long time, the whole of the ammonia may be driven off, leaving nothing but water in the retort.

Solution of ammonia is prepared on the large scale by mixing together in a capacious retort equal weights of sal ammoniac and well-burned quick-lime previously slaked and made into a paste with water. The retort is then connected with a series of bottles similar to those used for condensing nitric acid (399). The arrangement shown in fig. 313, which is an excellent one where a

FIG. 313.



liquid has to be saturated with any gas, may be employed for preparing a solution of ammonia on the small scale in the laboratory. The three-necked bottles, B, C, D, E, are known by the name of Woulfe's bottles: in the globe, A, a small quantity of water is placed, to retain any solid particles which may be mechanically carried over by the gas; in the first bottle, B (which should be kept cool by immersion in cold water), a quantity of water equal in weight to that of the sal ammoniac used is introduced, taking care that it shall not fill more than half the capacity of the bottle, whilst the second contains water to condense any gas that may escape through the first. Each bottle is provided with a safety tube open at both ends, so that if the gas were absorbed in B, for example, more rapidly than it was supplied, instead of the liquid being driven back from the bottle, C, air would enter by the safety tube, and the equilibrium would be restored. The tube

which delivers the gas passes down through the safety tube, and projects a little beyond its lower opening, so that the gas rises in bubbles through the liquid and collects in the bottle.

Solution of ammonia, if pure, should leave no solid residue when evaporated; the presence of carbonic acid may be detected by lime-water, which it renders milky; that of chlorine by acidulating slightly with pure nitric acid, and adding argentic nitrate, when a white cloud of argentic chloride is formed; that of sulphuric acid by a white precipitate with baric nitrate after dilution and saturation with nitric acid; that of lime by a white precipitate on adding ammonic oxalate; and that of copper or lead (derived from the apparatus used in its preparation) by a black or brown precipitate with sulphuretted hydrogen. Lead in small quantity is a very frequent impurity in the commercial solution and is usually derived from the action of the ammonia on the flint glass bottles in which it has been kept.

The ammoniacal salts will be described with those of the alkali metals, and the tests for ammonia will be given at the same time.

(393) **AMIDOGEN?** $NH_2 = 16$.—Ammonia is the only compound of hydrogen and nitrogen that has been obtained in the isolated form. When, however, potassium is heated gently in perfectly dry ammoniacal gas, the ammonia disappears, hydrogen is liberated, and a fusible, olive-green compound is formed, consisting of NKH_2. The ammonia is decomposed by the potassium in the following manner: $2\,NH_3 + K_2$ becomes $2NKH_2 + H_2$. This compound, NKH_2, may be considered either as ammonia, NH_3, in which one atom of hydrogen is replaced by the metal potassium, or as a compound of potassium with *amidogen*, NH_2. Those chemists who hold the latter view suppose that amidogen is capable of existing in combination with several metals and with a variety of bodies derived from the organic kingdom; it is far more convenient, however, in most cases, to regard these bodies as substitution-products formed upon the type of ammonia. Compounds of this class have received the name of *amides;* they will be considered hereafter.

(394) **AMMONIUM,** $NH_4 = 18$.—This compound, as is the case with amidogen, has not been obtained in a separate form. All the usual so-called salts of ammonia, however, may be regarded as containing it. Ammonic nitrate, for example, when formed by the action of ammonia on nitric acid, is not accompanied by any separation of the elements of water, which cannot be expelled from the salt by heat without entirely decomposing it (403); $NH_3 + HNO_3$ becoming $NH_4.NO_3$. Sal ammoniac is on this view regarded as ammonic chloride, $NH_4.Cl$. The full discussion of the grounds upon which this theory rests will be best postponed till we enter upon a description of the salts of ammonium.

(395) **HYDROXYLAMINE,** $NH_3O = 33$, $[NH_2(HO)]$.—By the action of reducing agents on nitrates, a base is formed having this composition: it may be regarded as intermediate between ammonia, NH_3, and ammonic hydrate, $NH_4.OH$, and is most

conveniently prepared by the action of tin and hydrochloric acid on an alkaline nitrite, or nitrate; preferably the ammonic salt. For this purpose Maumené (*Compt. Rend.*, 1870, lxx. 147) adds 55 parts of tin, in 3 or 4 portions, to 20 of ammonic nitrate in 217 of hydrochloric acid, of density 1·12, taking care to avoid any considerable rise of temperature; as soon as the reaction is complete, the tin is precipitated by sulphuretted hydrogen, and the solution evaporated at a gentle heat. The ammonic chloride crystallizes first, and then the very soluble hydroxylamine hydrochloride, which may be freed from the former by dissolving it in absolute alcohol, and precipitating the small amount of ammonic chloride present by platinic chloride. The concentrated alcoholic solution deposits the hydrochloride in long spicular crystals. Hydroxylamine hydrochloride may also be prepared by heating 5 parts of ethylic nitrate,* and 5 of hydrochloric acid, of density 1·12, with 12 of tin, or by passing nitric oxide through a series of vessels in which hydrogen is being evolved from tin and hydrochloric acid. Sodium amalgam may also be employed as a reducing agent (Lossen, *Zeits. Chem.*, 1865, i. 551; 1867, iii. 129; 1868, iv. 399).

Hydroxylamine is a very volatile base, which decomposes with great readiness, and has only been obtained in solution. It precipitates many metallic salts, such as those of lead, iron, nickel, and zinc. It is a powerful reducing agent, and when added to a solution of cupric sulphate, it throws down a grass-green precipitate, which yields cuprous oxide when boiled, with evolution of nitrous oxide. This is one of the most sensitive tests for hydroxylamine. Fehling's alkaline cupric solution gives a similar reaction with salts of hydroxylamine:

$$2NH_3O + 4CuO = 2Cu_2O + N_2O + 3OH_2.$$

(Donath, *Deut. chem. Ges. Ber.*, 1877, x. 766.) A solution of cupric sulphate, when heated with hydroxylamine hydrochloride, yields cuprous chloride; and an ammoniacal cupric solution is decolorized. It also reduces mercury, silver, gold, and platinum salts, throwing down the metals. *Hydroxylamine hydrochloride*, $NH_3O.HCl$, crystallizes from alcohol in long prisms resembling urea, and from water in six-sided tables. Hydroxylamine also forms crystalline hydrochlorides of the formula $2NH_3O.HCl$ and $3NH_3O.2HCl$, both of which are deliquescent, sparingly soluble

* It is also formed from other organic compounds (*Vid.* Meyer and Locker, *Deut. chem. Ges. Ber.*, 1875, viii. 215).

in alcohol, and insoluble in ether. The *nitrate* may be prepared from the hydrochloride by decomposing it with argentic nitrate. It is excessively soluble, and very difficult to obtain in the crystalline state. The *sulphate* is very soluble in water, but may be precipitated from its solution in needles by the addition of alcohol. When its solution is exactly decomposed by the equivalent quantity of baric hydrate, a solution of hydroxylamine is obtained. The *phosphate*, $(NH_3O)_3.H_3PO_4$, is but sparingly soluble in cold water, and separates in small cubic crystals on adding sodic phosphate to a moderately concentrated solution of hydroxylamine hydrochloride.

(396) **CHLORIDE OF NITROGEN** ($NHCl_2.NCl_3$?); *Density of Liquid*, 1·653.—The attraction existing between chlorine and nitrogen is very feeble; the compound commonly known by the name of chloride of nitrogen is always obtained by indirect means.

If a current of ammoniacal gas be directed into a bottle of gaseous chlorine, it will take fire spontaneously, burning with a green flame, whilst hydrochloric acid is formed, and nitrogen is set free; dense white fumes being generated by the union of the hydrochloric acid with undecomposed ammonia. By modifying the experiment, the reaction may be employed as a means of obtaining nitrogen gas, for when a stream of chlorine gas is passed through a solution of ammonia, the hydrochloric acid as fast as it is formed combines with the excess of ammonia, whilst nitrogen is liberated: if the solution be concentrated, each bubble of chlorine produces a flash of light. Two molecules of ammonia, when decomposed by three molecules of chlorine, yield one molecule of nitrogen and six of hydrochloric acid; $2NH_3 + 3Cl_2$ becoming $6HCl + N_2$. The nitrogen is apt to be mixed with a variable quantity of oxygen, a little water being also decomposed at the same time (A. Anderson).

But if instead of acting on a solution of free ammonia, a bottle of chlorine perfectly free from greasy matter be inverted over a leaden dish containing a solution of 1 part of sal ammoniac, NH_4Cl, in 12 parts of water, drops of a yellow, oily-looking liquid gradually collect on the surface of the solution and fall to the bottom, whilst the chlorine slowly disappears; this liquid is the substance known as *chloride of nitrogen*. A safer method of obtaining this body consists in suspending a fragment of sal ammoniac (say 1·5 or 2 grams) in a solution of hypochlorous acid; oily drops of the so-called chloride of nitrogen are gradually formed, and sink in the liquid as the salt is dissolved. It may

also be readily prepared by decomposing a saturated solution of ammonic chloride by means of the electric current from four or five cells of Bunsen's battery. The solution is placed in a funnel, the neck of which is cut off short and stopped with a cork, through which the wires pass connecting the platinum electrodes with the battery. If a little turpentine be poured on the surface so as to form a thin layer covering the liquid, each bubble of the chloride of nitrogen as it is formed and rises to the surface of the dense solution will explode harmlessly. The new body remains liquid at -27° ($-16^\circ{\cdot}6$ F.), but is very volatile, and possesses a peculiar penetrating odour. It is one of the most dangerous compounds known, for it explodes with tremendous violence when heated to between 93° and 100° (200° and 212° F.), emitting a flash of light when the detonation occurs. The explosion is so sudden that it invariably breaks any glass or porcelain vessel in which it may be contained: hence a leaden saucer is used in preparing the compound. The liquid chloride also explodes violently at ordinary temperatures when brought into contact with many inflammable substances, such as oil of turpentine, phosphorus, and the fixed oils. The alkalies likewise cause its immediate explosion. On the other hand, it does not explode when touched with strong acids, with metallic bodies in general, with the resins, or with sugar.

Little or nothing is known of the cause of these remarkable reactions, or of the light and heat emitted when the chloride explodes by slight elevation of temperature; in this case, and in the analogous instances of the explosion of the oxides of chlorine, light is emitted, not during an act of combination, as usual, but during the expansion and sudden separation of the two gaseous elements.

The analysis of this body is attended with great difficulty. It is a substitution product obtained from ammonia, the hydrogen of which has been more or less completely displaced by chlorine; and it is highly probable that it is not simply a chloride of nitrogen, but a combination of chlorine, nitrogen, and hydrogen, $NHCl_2.NCl_3$, somewhat analogous to the corresponding explosive compounds obtained by the action of iodine on ammonia (466).

§ II. OXIDES AND OXACIDS OF NITROGEN.

(397) The attraction of nitrogen for oxygen is much feebler than that of either carbon or hydrogen for oxygen, so that it is not easy to effect their direct union; but, indirectly, five distinct compounds of nitrogen with oxygen have been obtained, the composition of which is given in the following table:

		By weight. N.	O.	In 100 parts. Nitrogen.	Oxygen.	Mol. Vol.
Nitrous oxide ...	N_2O = 44	or 28	+ 16	63·64	+ 36·36	
Nitric oxide ..	NO = 30	14	+ 16	46·67	+ 53·33	
Nitrous anhydride	N_2O_3 = 76	28	+ 48	36·84	+ 63·16	P
Peroxide of nitrogen	N_2O_4 = 92	28	+ 64	30·44	+ 69·56	
Nitric anhydride...	N_2O_5 = 108	28	+ 80	25·93	+ 74·07	P

(398) **NITRIC ANHYDRIDE**, or *Dinitric Pentoxide*, N_2O_5 $\left[\begin{matrix}NO_2\\O\\NO_2\end{matrix}\right]$;—*Fusing-pt.* 29°·5 (85° F.); *Boiling-pt.* 45° (113° F.); *Density of solid* 1·64.—This substance, which is a very unstable compound, forms transparent, brilliant, colourless crystals, derived from the right rhombic prism; they melt at 29°·5 (85° F.), and boil at 45° (113° F.), undergoing decomposition at this temperature. The crystals may be kept for some days at 10° (50° F.), but they decompose readily at the ordinary temperature into oxygen and nitric peroxide, especially if exposed directly to the rays of the sun, so that if preserved in sealed tubes the pressure exerted by the liberated gases soon bursts the tube with a dangerous explosion. The anhydride is readily volatile, condensing in beautiful crystals on the cooler part of the tube or bottle containing it. The crystals are dissolved rapidly by water, emitting much heat, and producing ordinary hydrated nitric acid.

In order to procure the anhydride, a uniform current of perfectly dry chlorine gas is passed very slowly over crystals of well-dried argentic nitrate; the salt is at first heated to about 95° (203° F.) until the decomposition has commenced, and the temperature is then lowered to about 60° (140° F.). The operation is one of considerable delicacy, and requires attention to a number of minute precautions, for the details of which the reader is referred to Deville's paper (*Ann. Chim. Phys.*, 1850 [3], xxviii. 241). The chlorine displaces the nitrion, NO_3, from the argentic nitrate; argentic chloride is formed, and the nitrion breaks up into nitric anhydride whilst oxygen escapes. By surrounding the receiver with a freezing mixture, the nitric anhydride is condensed in crystals. The decomposition may be represented in the following manner, although it is probably not quite so simple:*

* It is possible that nitrylic chloride, NO_2Cl, is first formed thus: $2AgNO_3 + 2Cl_2 = 2AgCl + 2NO_2Cl + O_2$, and then that this chloride decomposes a second molecule of argentic nitrate; $AgNO_3 + NO_2Cl = AgCl + N_2O_5$: this is rendered more probable from the experiments of Odet and Vignon, who find that nitric anhydride may be readily prepared by passing the vapour of nitrylic chloride over dry argentic nitrate heated to a temperature of about 65° (149° F.).

$$4AgNO_3 + 2Cl_2 \text{ give } 4AgCl + O_2 + 2N_2O_5.$$
Argentic nitrate. Argentic chloride. Nitric anhydride.

Nitric anhydride can also be prepared by cautiously adding phosphoric anhydride to nitric acid cooled by a freezing mixture and subsequently distilling the mixture. (Weber, *Pog. Ann.*, 1872, cxlvii. 113). Berthelot (*Jour. Pharm.*, 1874 [4], xix. 182, and *Bull. Soc. Chim.*, 1874 [2], xxi. 53)' has succeeded in obtaining from the acid more than 60 per cent. of its weight of anhydride by slightly modifying the details of this method. He adds to the strongest nitric acid, cooled in a mixture of ice and salt, rather more than its own weight of phosphoric anhydride, taking care that the temperature does not rise above 0° (32° F.). The pasty mass thus obtained is transferred to a tubulated retort capable of containing five or six times the quantity, and very slowly and cautiously distilled, the neck of the retort being surrounded with ice, and the retort itself occasionally placed in a freezing mixture to prevent too rapid action. The anhydride condenses in long transparent colourless crystals, which when exposed to the air slowly evaporate without deliquescing.

Deville ascertained the composition of nitric anhydride by estimating the quantity of nitrogen which a given weight of the compound furnished after removal of the oxygen by passing the vapour over finely divided metallic copper at a high temperature; 100 parts by weight of the anhydride were thus found to contain 25·9 of nitrogen; the deficiency, 74·1, is oxygen; or 28 parts of nitrogen are united with 80 of oxygen.

(399) **NITRIC ACID**; *Hydric Nitrate,* HNO_3 [$NO_2(OH)$] =63; *Density of Liquid at* 15° (59° F.) 1·530, *at* 0° (32° F.) 1·559; *Boiling-pt.* 86° (187° F.); *Comp. in* 100 *parts,* N_2O_5, 85·72; OH_2 14·28.—The most important of the compounds of oxygen with nitrogen is that which when in combination with water was formerly called *aqua fortis,* and is now designated nitric acid. It was known to the alchemists, but its true composition was first determined by Cavendish in 1785. When nitrogen is mixed with 12 or 14 times its bulk of hydrogen, and a jet of the mixed gas is allowed to burn in air or in oxygen, the water which is formed has a sour taste and an acid reaction, owing to the simultaneous formation of a small quantity of nitric acid. In this case the nitrogen burns by the aid of the heat developed during the combustion of the hydrogen, and the oxidized compound combines at once with the water formed, which much increases its chemical stability. It was, indeed, owing to the accidental production of nitric acid in the course of his

experiments on the formation of water by the combustion of hydrogen, that Cavendish was induced to institute the train of researches which terminated in this important discovery.

If a mixture of 2 volumes of nitrogen with 5 volumes of oxygen be introduced into the bent eudiometer (fig. 287) the tube of which is filled up with an infusion of blue litmus in distilled water, and a series of sparks be passed through the gaseous mixture by means of an induction coil, the two gases will combine gradually, and the litmus solution will be reddened. The heat of the spark determines the combination of the gases just at the spot through which it passes, but the action does not extend further. In like manner, if a number of sparks from the electrical machine be passed between two metallic points, over moistened litmus-paper, a red spot will be produced upon the paper, owing to the formation of a minute quantity of nitric acid by the combination of the oxygen and nitrogen of the air in presence of aqueous vapour. During stormy weather, and indeed whenever a flash of lightning passes through a moist atmosphere, the same compound is produced in appreciable quantity, so that it is rare to meet with rain water in which traces of ammonic nitrate may not be detected, if it be examined by sufficiently delicate processes. Ammonia likewise yields nitric acid under certain circumstances by slow oxidation (391).

Nitrates of potassium and sodium occur in the form of an efflorescence on the soil, especially in tropical climates, as in some parts of India and Peru. The compound formed with potassium constitutes the nitre or saltpetre of commerce. The nitrates of the alkali-metals are often present in the water of wells in towns or in the vicinity of cemeteries, the nitric acid being in these cases produced by the oxidation of azotized animal matters, as they undergo decomposition during the percolation of their aqueous solution through the soil.

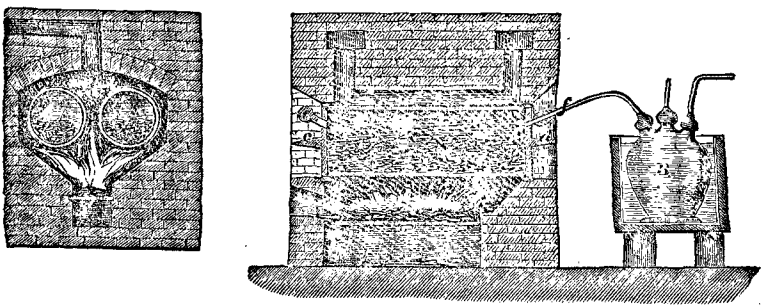
Preparation.—It is from one of these nitrates that the acid is always obtained for chemical purposes. When potassic nitrate is heated with a powerful acid, such as the sulphuric (H_2SO_4, dihydric sulphate), a true double decomposition occurs. The potassium and hydrogen change places, forming on the one hand hydric potassic sulphate, $KHSO_4$, and on the other hydric nitrate, or nitric acid, HNO_3. The hydric potassic sulphate remains in the retort, whilst the more volatile nitric acid distils over, and may be condensed in the usual manner. The method of preparing nitric acid offers a good example of the general principle upon which acids which admit of being distilled without experiencing decom-

position are obtained from their metallic salts; the ordinary acids, it must be remembered, are *salts of hydrogen*. In preparing nitric acid on the small scale, equal weights of nitre and oil of vitriol are placed in a glass retort, and the distillation is proceeded with in the manner shown in figs. 143 and 144, Part I. p. 393.

During the distillation, red fumes appear in the retort, arising from a partial decomposition of the acid, and the formation of some of the lower oxides of nitrogen, whilst a yellowish corrosive liquid is condensed in the receiver: this liquid is hydric nitrate, or concentrated nitric acid, HNO_3; it fumes strongly in the air and emits a powerfully irritating, and acid odour.

On the large scale, iron retorts, fig. 314, coated with fire-clay on the inside of the upper part, where they are exposed to the acid vapours, are employed for the distillation, and sodic nitrate is substituted for potassic nitrate, as it is a

1. FIG. 314. 2.



cheaper salt, and likewise yields 9 per cent. more nitric acid than potassic nitrate. The cylinders or retorts are arranged in pairs in a furnace, so that each fire heats two cylinders, as shown in the section, 1. The cylinders are supplied with a moveable lid, *c*, *d*, at each end. The nitrate is introduced into the retort, A, through the opening at *c*, which is closed during the distillation by a stone lid, fitted accurately to the aperture; and the oil of vitriol (usually chamber acid) is added by a funnel at *e*, after the retort is closed. As soon as the acid is introduced, the funnel is withdrawn, and the opening at *e* is closed with a plug. The nitric acid as it distils over passes through the pipe *f*, and is condensed in a series of stoneware bottles, the first of which is seen at B. The acid collected in the first receiver is always contaminated with sulphuric acid, and that in the last is rather dilute, as water is placed in it to condense the nitrous fumes.

Upon the large scale, it is customary to employ a proportion of sulphuric acid smaller than that used when the distillation is performed in glass vessels, for it is quite possible to effect a complete decomposition of the nitrate by heating it with one-half its weight of oil of vitriol. Under these circumstances, however, a higher temperature is needed to expel the last portions of acid, and a considerable quantity of the nitric acid is thereby decom-

posed and wasted. The residue in the retort, when the smaller quantity of sulphuric acid is used, is dipotassic sulphate, K_2SO_4, which is much less soluble in water, and consequently is much more difficult of removal: but in the iron cylinder of the manufacturer this is of no moment, because the saline mass can easily be detached by the use of iron tools when the distillation is at an end.

The cause of these differences in the result of the processes adopted on the large and on the small scale lies in the fact that sulphuric acid by its reaction upon potash gives rise to two different sulphates, one of which contains twice as much potassium as the other; the acid sulphate, consisting of $KHSO_4$, being a hydric potassic sulphate, whilst the common neutral sulphate, or dipotassic sulphate contains K_2SO_4.

When nitre and sulphuric acid are mixed in the proportion of equal weights (or 1 molecule of nitre, to 1 of acid), the hydric potassic sulphate is obtained, and nitric acid distils readily; half the hydrogen only of the sulphuric acid being displaced by potassium; the change is represented in the following equation:

$$\underset{\text{Nitre.}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Nitric}\\\text{acid}}}{HNO_3} + \underset{\substack{\text{Hydric potassic}\\\text{sulphate.}}}{KHSO_4};$$

$$[\mathbf{N}O_2(OK) + \mathbf{S}O_2(OH)_2 = \mathbf{N}O_2(OH) + \mathbf{S}O_2(OH)(OK);]$$

but if the nitrate be mixed with sulphuric acid in the proportion of two molecules of the former to one of the latter, the decomposition takes place in two successive stages; in the first of these, half the nitre only is decomposed, hydric potassic sulphate being furnished in the first instance as before, and a gentle heat only is needed for the distillation of the nitric acid so produced. The following equation represents this first stage of the change:

$$2\underset{\text{Nitre.}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\text{Nitre.}}{KNO_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{HNO_3} + \underset{\substack{\text{Hydric potassic}\\\text{sulphate.}}}{KHSO_4}.$$

$$[2\mathbf{N}O_2(OK) + \mathbf{S}O_2(OH)_2 = \mathbf{N}O_2(OK) + \mathbf{N}O_2(OH) + \mathbf{S}O_2(OH)(OK).]$$

But as soon as the first half of the nitric acid has passed over, the temperature begins to rise, and the hydric potassic sulphate reacts on the undecomposed nitre; the second half of the nitric acid is then formed, but is at the same time partially decomposed, owing to the high temperature, and this is particularly the case towards the end of the operation: finally, the whole of the potassium remains in the retort in the form of the sparingly soluble neutral

or dipotassic sulphate. This second stage of the decomposition is exhibited in the subjoined equation :

$$\underset{\text{Nitre.}}{KNO_3} + \underset{\substack{\text{Hydric potassic}\\ \text{sulphate.}}}{KHSO_4} = \underset{\substack{\text{Nitric}\\ \text{acid.}}}{HNO_3} + \underset{\substack{\text{Dipotassic}\\ \text{sulphate.}}}{K_2SO_4.}$$

$$[NO_2(OK) + SO_2(OH)(OK) = NO_2(OH) + SO_2(OK)_2.]$$

Similar equations would represent the reactions with sodic nitrate, substituting the symbol Na for K, wherever the latter occurs.

Properties.—The acid which is obtained by the foregoing process is of a yellowish or red colour, owing to the presence of some of the lower oxides of nitrogen ; these may, if necessary, be removed by mixing the acid with an equal bulk of oil of vitriol, and submitting the mixture to distillation. If the first portions be collected, and a current of dry air be passed through the liquid, gently warmed and sheltered from strong daylight, a pure acid remains behind as colourless as water, and quite free from the lower oxides of nitrogen. It is, however, so unstable in this concentrated form that it cannot be redistilled without undergoing partial decomposition. When exposed to the sun's light, a similar decomposition takes place ; oxygen gas is evolved, and the acid becomes coloured from the formation of lower oxides of nitrogen. When pure, nitric acid is a colourless, limpid, fuming, powerfully corrosive liquid, which freezes at about $-55°$ ($-67°$ F.). It begins to boil at $86°$ ($187°$ F.), but the temperature rises gradually, owing to the decomposition of the liquid ; oxygen and nitrous fumes are evolved ; the boiling-point continues to rise slowly until it reaches $121°$ ($250°$ F.), at which point the acid in the retort distils unchanged, and has a composition approaching to, $2HNO_3.3OH_2$.*

Owing to the facility with which the acid parts with oxygen, it is continually employed as an oxidizing agent. If it be dropped on to hot finely powdered charcoal, the charcoal burns vividly ; mixed with a little oil of vitriol, and poured into oil of turpentine, the mixture bursts into flame. Sulphur and iodine are oxidized by it, and phosphorus almost with explosive violence. Nitric acid is one of the most corrosive substances known, it destroys all animal textures rapidly, and if slightly diluted stains the skin, wool, feathers, and all albuminous bodies of a bright yellow colour. Nitric acid acts violently upon tin or iron filings, espe-

* Like hydrochloric, sulphuric, and other acids, the composition of nitric acid of constant boiling point, varies with the pressure (*note*, p. 32).

cially if they be previously moistened with a few drops of water; and attacks most of the other metals except gold, platinum, rhodium, and iridium. The action of nitric acid upon the metals varies with its temperature and degree of dilution: but its energy is most manifest when diluted to a density of from 1·35 to 1·25. The pure concentrated acid, HNO_3, is in fact without action upon tin, iron, bismuth, and many other metals at ordinary temperatures. The presence of nitrous acid in the nitric acid greatly increases its oxidizing power, as, owing to the instability of nitrous acid, this compound parts with its oxygen very readily. At a temperature of $-18°$ (0°·4 F.), the acid, whether concentrated or dilute, is without action on copper, but it dissolves zinc rapidly.

(400) **Action of Nitric Acid on Metals.**—The chemical action of nitric acid upon the metals is a process of considerable importance, but in order to study with advantage the effects to which it gives rise, it will be useful to consider the action of acids upon the metals from a general point of view. It has already been stated that the metals unite directly with many of the non-metallic elements, such as chlorine and oxygen. Antimony, for example, will take fire spontaneously if allowed to fall in fine powder into chlorine, and iron will burn in oxygen if first heated to the point of ignition. The metallic oxides, in contact with dilute acids, become quickly dissolved; cupric oxide is dissolved by dilute sulphuric acid, zincic oxide quickly disappears when agitated with hydrochloric acid, and plumbic oxide is rapidly dissolved by acetic acid.

But a metal will not unite directly with an anhydride. Union between a metallic oxide and an anhydride may, however, occur, although, even then, the action is much favoured by the presence of water. Sulphuric anhydride, for instance, does not act upon iron, but the anhydride is immediately absorbed by potassic hydrate, $KHO+SO_3$ becoming $KHSO_4$; and in like manner, carbonic anhydride is rapidly absorbed by slaked lime (calcic hydrate).

When the metals are placed in contact with the acids, other phenomena are observed; a brisk action frequently takes place, accompanied by the evolution of a gas, and it is very often stated that the metal first becomes oxidized, and is then dissolved by the acid. It is not, however, necessary to assume that the metal undergoes oxidation as a preliminary step, for the reaction may be explained on the supposition that the metal simply displaces the hydrogen of the acid. When, for example, zinc is

placed in dilute sulphuric acid, the metal is rapidly dissolved, whilst hydrogen escapes in the gaseous form; $H_2SO_4 + Zn$ yielding $ZnSO_4 + H_2$. A similar result is obtained when iron or tin is dissolved in hydrochloric acid, ferrous or stannous chloride being produced, whilst hydrogen is given off, the reaction in the case of iron being represented by the equation $2HCl + Fe = FeCl_2 + H_2$. When an oxide is employed instead of a metal, the hydrogen, instead of escaping as gas, is eliminated in the form of water; for instance, in the action of zincic oxide upon sulphuric acid, the change may be represented as $ZnO + H_2SO_4 = ZnSO_4 + OH_2$; and again with cupric oxide and hydrochloric acid,

$$CuO + 2HCl = CuCl_2 + OH_2.$$

The ordinary action of metals upon sulphuric acid, in which the components of the acid are united by powerful chemical ties, is, as we have just seen, comparatively simple; but where the elements of the acid are but feebly held together, as is the case with nitric acid, the actions are often more complicated. When, for example, silver or copper is dissolved in nitric acid, hydrogen may as before be displaced from the acid by the metal which becomes dissolved; although, owing to the facility with which nitric acid parts with its oxygen, no hydrogen is set free, but at the moment of its liberation reduces the nitric acid with formation of one or more of the lower oxides of nitrogen, and in some cases of a salt of ammonia or hydroxylamine; it is these oxides of nitrogen which occasion the ruddy fumes usually observed when a metal is dissolved in nitric acid. The exact nature of the decomposition, however, varies in different cases; silver when allowed to dissolve slowly in the cold in an excess of diluted nitric acid produces nitrous acid, HNO_2, which remains in solution, whilst nitric oxide, NO, is given off in small quantity; $Ag_2 + 3HNO_3$ giving $2AgNO_3 + OH_2 + HNO_2$. With metals which attack the acid more vigorously, such as copper or mercury, nitric acid of moderate concentration (density 1·25 to 1·3) disengages nitric oxide in large quantity together with nitrous oxide, and some nitrogen; the amount of the two last mentioned being largely increased when a more dilute acid is employed; for example, $3Cu + 8HNO_3$ yields $2NO + 3(Cu2NO_3) + 4OH_2$; but if the acid be more highly concentrated (density 1·42), peroxide of nitrogen is disengaged abundantly; $Cu + 4HNO_3$ yielding $Cu2NO_3 + 2NO_2 + 2OH_2$. And when the decomposition occurs at a high temperature, free nitrogen is usually disengaged in considerable quantity, the acid undergoing complete deoxida-

tion; $5Cu+12HNO_3=5(Cu2NO_3)+N_2+6OH_2$. If the metal, like zinc, has a still more energetic action, the dilute acid yields nitrous oxide in large quantity amongst the gaseous products; $4Zn+10HNO_3=N_2O+4(Zn2NO_3)+5OH_2$. When zinc or tin is used with a stronger acid, ammonia (and probably hydroxylamine also) is found amongst the products; for instance, $4Zn+9HNO_3=4(Zn2NO_3)+3OH_2+NH_3$, the ammonia combining with the excess of acid employed. (Deville. *Compt. Rend.*, 1870, lxx. 22, 550; Acworth and Armstrong, *Jour. Chem. Soc.*, 1877, ii. 54).

Strength of Nitric Acid (*J. Kolb, Ann. Chim. Phys.*, 1867 [4], x. 136).

HNO_3 in 100 parts by weight.	Density.		HNO_3 in 100 parts by weight.	Density.	
	at 0° (32° F.)	at 15° (59° F.)		at 0° (32° F.)	at 15° (59° F.)
100·00	1·559	1·530	56·10	1·371	1·353
99·52	1·557	1 529	54·00	1·359	1·341
97·00	1·548	1·520	52·33	1·349	1·331
96·00	1·544	1·516	49·97	1·334	1·317
94·00	1·537	1·509	47·18	1·315	1·298
92·00	1·529	1·503	45·00	1·300	1·284
91·00	1·526	1·499	43·53	1·291	1·274
90·00	1·522	1·495	40·00	1·267	1·251
88·00	1·514	1·488	37·95	1·253	1·237
86·17	1·507	1·482	33·86	1·226	1·211
84·00	1·499	1·474	30·00	1·200	1·185
82·00	1·492	1·467	28·00	1·187	1·172
80·00	1·484	1·460	25·71	1·171	1·157
77·66	1·476	1·451	23·00	1·153	1·138
75·00	1·465	1·442	20·00	1·132	1·120
72·39	1·455	1·432	17·47	1·115	1·105
69·20	1·441	1·419	15·00	1·099	1·089
67·00	1·430	1·410	13·00	1·085	1·077
65·07	1·420	1·400	11·41	1·075	1·067
63·59	1·413	1·393	7·22	1·050	1·045
61·21	1·400	1·381	4·00	1·026	1·022
59·59	1·391	1·372	2·00	1·013	1·010

The preceding table indicates the percentage of nitric acid, HNO_3, contained in aqueous solutions of various specific gravities.

(401) **Hydrates of Nitric Acid.**—When concentrated nitric acid is exposed to the air, it absorbs moisture, and if 70 parts of the concentrated acid be mixed with 30 of water, it emits a sensible amount of heat. Under these circumstances a hydrate of nitric acid of considerable stability appears to be formed with

a composition approximately represented by the formula, $2HNO_3.3OH_2$: such an acid has a density of 1·424; it boils at 121° (250° F.), and may be distilled, under ordinary pressures apparently unaltered. A weaker acid when heated parts with its water until it arrives at this density, and a stronger acid, when distilled, loses acid until reduced to this point, the liquid in the retort eventually, in both cases, acquiring a density of 1·424. Although this hydrate does not vary sensibly in composition when distilled under the ordinary atmospheric pressure, Roscoe found by conducting the distillation at reduced pressures, that the density of the acid in the retort, and consequently the proportion of water, varies with the pressure under which the distillation takes place. A hydrate of the composition, $N_2O_5.2HNO_3$, analogous to pyrosulphuric acid, $SO_3.H_2SO_4$, is formed by dissolving the requisite quantity of the anhydride in nitric acid. It may be obtained in crystals.

(402) **Common Impurities of Nitric Acid.**—The nitric acid of commerce is liable to be contaminated with a variety of foreign matters, of which sulphuric acid, chlorine, potash, and oxide of iron are the most frequent. Commercial nitric acid prepared from sodic nitrate, almost always contains minute traces of iodine. Its usual yellow or red colour is owing to the presence of some of the lower oxides of nitrogen. The pure acid leaves no fixed residue when evaporated on a watch glass, and gives no precipitate when, after dilution with three or four times its bulk of water, it is tested for sulphuric acid with baric nitrate, $Ba2NO_3$, and for chlorine with argentic nitrate. By distilling it a second time, it may readily be obtained of a density 1·42, and free from all impurities except the lower oxides of nitrogen. Before rectification, if chlorine or iodine be present, argentic nitrate should be added so long as the silver salt occasions a precipitate, or a silver coin may be dissolved in the acid. The lower oxides of nitrogen may be removed by diluting the acid with water until of a density not exceeding 1·42, and then distilling with 2 or 3 per cent. of potassic dichromate.

Nitrates.—Nitric acid is monobasic; that is to say, it contains only one atom of hydrogen capable of being displaced by an atom of a monad metal like potassium; the salts which it forms are termed *nitrates*. Their general formula is $M'NO_3$. These salts may be obtained without difficulty by dissolving either the metal itself, or its oxide, or its carbonate, in nitric acid more or less diluted. Many of the nitrates, including potassic, sodic, ammonic, baric, plumbic, and argentic nitrates,

are anhydrous. Others combine with 6 molecules of water of crystallization: among these are the salts of magnesium, zinc, nickel, cobalt, iron, and copper; whilst in others the proportion of the water is different, calcic nitrate retaining $4OH_2$, and strontic nitrate $5OH_2$. If crystallized at a high temperature, cupric nitrate retains only $3OH_2$, and strontic nitrate may be obtained in the anhydrous form. No acid nitrates are known, but several subnitrates or basic nitrates exist; that is to say, salts may be formed which contain more than one equivalent of basyl for each equivalent of acid radicle: such, for instance, as the hydrated basic nitrate of copper, $Cu_2NO_3.3CuH_2O_2$.

The following table gives the composition of some of the nitrates:

Potassic nitrate	KNO_3
Sodic nitrate	$NaNO_3$
Ammonic nitrate	NH_4NO_3
Baric nitrate	Ba_2NO_3
Strontic nitrate	$Sr_2NO_3.5OH_2$
Calcic nitrate	$Ca_2NO_3.4OH_2$
Magnesic nitrate	$Mg_2NO_3.6OH_2$
Zincic nitrate	$Zn_2NO_3.6OH_2$
Ferrous nitrate	$Fe_2NO_3.6OH_2$
Cupric nitrate	$Cu_2NO_3.6OH_2$
Plumbic nitrate	Pb_2NO_3
Argentic nitrate	$AgNO_3$
Mercurous nitrate	$HgNO_3.OH_2$
Hydrated plumbic subnitrate	$Pb_2NO_3.PbH_2O_2$
Hydrated cupric subnitrate	$Cu_2NO_3.3CuH_2O_2$
Hydrated mercurous subnitrate	$3HgNO_3.Hg_2O.OH_2$

Most of the nitrates fuse readily when heated, and at an elevated temperature they are all decomposed. From the nitrates of the alkali-metals, nearly pure oxygen escapes at first, and a nitrite is formed, but afterwards the nitrite undergoes decomposition, a mixture of oxygen and nitrogen passes off, and the oxide of the metal is left. When thrown on glowing coals, the nitrates are decomposed with deflagration: if paper be moistened with a solution of any nitrate, allowed to dry, and then ignited, it will burn with the rapid, smouldering combustion characteristic of touch-paper. This property is also exhibited by the salts of some other acids, the chlorates being the most important.

All the nitrates, when heated with sulphuric acid, evolve nitric acid; but there is no ready method of precipitating nitric acid from its solutions, since all its compounds are more or less soluble in water. Various indirect methods have been proposed for ascertaining its presence: one of the best of these consists in

neutralizing the solution, if acid, with potassic hydrate, and evaporating nearly to dryness, then adding a few copper clippings, and heating the mixture with a little concentrated sulphuric acid; if nitric acid be present, the characteristic red fumes of peroxide of nitrogen will make their appearance. A quantity of these fumes, too small to be visible, may be detected by suspending in the vessel a piece of paper moistened with a mixture of starch and solution of potassic iodide (p. 53), which will become blue from the formation of a compound of the starch with the liberated iodine. The most delicate test for nitric acid, however, is ferrous sulphate; if a small quantity of this salt be dissolved in the solution to be tested, and sulphuric acid be cautiously poured down the side of the tube containing the mixture so as to form a distinct stratum below it, a brownish-red coloration will make its appearance at the line of contact between the two liquids if nitric acid be present; this depends upon the circumstance that the nitric oxide which is formed by the deoxidizing action of one portion of the iron salt, becomes dissolved with the distinctive brown colour, in the solution of the unaltered part of the ferrous salt; the deoxidation of the nitric acid which occurs may be represented in the following equation:

$$\underset{\text{Ferrous sulphate.}}{6FeSO_4} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Ferric sulphate.}}{3(Fe_2 3SO_4)} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{4OH_2}.$$

If a few drops of hydrochloric acid be added to a solution which contains free nitric acid or a nitrate in solution, the liquid acquires the power of dissolving gold leaf. This effect, however, is produced by hydrochloric acid in solutions of the chlorates, bromates, and iodates, so that the absence of these acids must be proved before applying this test (361, 455, 464).

The accurate quantitative determination of nitric acid when mixed with other acids is a matter of considerable difficulty. One method consists in the conversion of the acid into ammonia, and the subsequent determination of the amount of ammonia found (391). Another, which, when the quantity of nitric acid is very small, furnishes excellent results, is that proposed by Pugh (*Jour. Chem. Soc.*, 1859, xii. 35). It is based upon the determination of the amount of stannous chloride which is converted into stannic chloride when the solution is heated with nitric acid in presence of an excess of hydrochloric acid. A certain quantity of the concentrated solution containing the nitric acid to be determined is introduced into a strong tube, and a known volume of a solution of stannous chloride in a large excess of hydrochloric acid is added, the strength of the tin solution having been ascertained by the use of a standard solution of potassic dichromate. Care is taken to employ an excess of the tin solution. A fragment of marble is dropped into the tube so as to produce a quantity of carbonic anhydride sufficient to displace the atmospheric air. The tube is then carefully sealed and exposed for about a quarter of an hour to a temperature of

170° (338° F.). It is allowed to cool, and the contents of the tube are next transferred to a glass and diluted with 90 or 100 cub. centim. of water: a few drops of a weak solution of potassic iodide and starch are then added, and the amount of tin still remaining in the form of stannous salt is determined by the addition of a graduated solution of the dichromate, until the liquid becomes blue from the liberation of iodine. The reaction upon which this process depends may be thus expressed:

$$HNO_3 + 4SnCl_2 + 9HCl = NH_4Cl + 4SnCl_4 + 3OH_2;$$

the nitrogen of the nitric acid being wholly converted into ammonia during the operation: the difference between the amount of the dichromate originally required to peroxidize the quantity of tin solution employed, and that actually consumed after the experiment is over, yielding the data for fixing the quantity of nitric acid: 393·3 mgrms. of the dichromate represent 63 of nitric acid, HNO_3, or 54 of the anhydride, N_2O_5. This method, however, is not applicable for determining the nitrates in water analysis, as the organic matter present interferes with the result.

(403) **NITROUS OXIDE**, *Protoxide of Nitrogen, or Nitrogen Monoxide*; $N_2O=44$. [ON_2.] *Mol. Vol.* [ ]; *Rel. wt.* 22; *Theoretic Density* 1·5224; *Observed Density* 1·527.—*Preparation.*—1. If a mixture of equal parts of nitric and sulphuric acids, diluted with 8 or 10 parts of water, be digested with metallic zinc, the metal displaces the hydrogen of the sulphuric acid, which at the moment of its liberation deoxidizes the nitric acid, and a colourless gas is slowly given off, composed of 2 atoms of nitrogen united with 1 atom of oxygen.

2.—But to obtain the gas in a pure state, it is far better to heat ammonic nitrate (NH_4NO_3, the salt furnished by neutralizing pure nitric acid with ammonic carbonate) in a glass retort; the salt quickly melts, and at a temperature of between 200° and 260° (392° and 500° F.) apparently begins to boil, although in reality it is undergoing decomposition, being resolved into the gaseous nitrous oxide and aqueous vapour. The operation must be carefully watched, and the temperature not be allowed to rise so high as to occasion the production of white vapours in the retort, because the decomposition is then apt to occur with explosive violence. The reaction may be explained as follows:—Ammonium is a compound of nitrogen with hydrogen; when the ammonic nitrate is heated, the hydrogen of the ammonium combines with part of the oxygen of the nitrion, forming water, whilst the remaining atom of oxygen unites with the two atoms of nitrogen, forming nitrous oxide. The result is that the whole of the nitrogen, both of the nitrion and of the ammonium, is liberated in the form of nitrous oxide: NH_4NO_3 becoming $2OH_2 + N_2O$ [$NO_2(ONH_4) = ON_2 + 2OH_2$]; 1 ounce or 30 grams

of the salt furnishes about 500 cubic inches, or rather more than 8 litres of the gas.

3.—L. Smith adopts a modification of the foregoing process for preparing the gas: he decomposes ammonic chloride, NH_4Cl, by means of nitric acid (of density 1·20) at a gentle heat. The gas which is obtained in this manner is not pure, but is contaminated with small quantities of chlorine and of nitrogen; the chlorine may be removed by allowing the gas to bubble up through a solution of potash. Advantage may sometimes be taken of this action of nitric acid on sal ammoniac to destroy an excess of ammonic chloride in solution in the course of an analysis.

Properties.—Nitrous oxide is a transparent, colourless gas, with a faint sweetish smell and taste, and is readily decomposed into its elements, under the action of the silent electrical discharge: 100 volumes of water at 0° (32° F.) dissolve 130·5 of the gas; at 15° (59° F.), 77 vols.; and at 24° (75° F.) only 60·8 vols. (Bunsen). Owing to this considerable diminution in solubility with the rise of temperature, it should be collected over warm water. Under a pressure of 50 atmospheres at 7° (45° F.), it is reducible to a colourless liquid, whose density at 0° (32° F.), is 0·9004 (Wills), [according to Andréeff (*Ann. Chem. Pharm.*, 1859, cx. 1) it has a density of 0·9370 at 0° (32° F.), 0·8964 at 10° (50 F.), and 0·8704 at 15° (59° F.)]. It boils at about −92° (−133° F.) (Wills, *Jour. Chem. Soc.*, 1874, xxvii. 21), and may be frozen into a transparent solid which melts at −99° (−146° F.). When the liquid nitrous oxide was mixed with carbonic bisulphide, and exposed to evaporation *in vacuo*, Natterer obtained a reduction of temperature which he estimated at −140° (−220° F.); this is a lower point than has hitherto been attained by any other means. The gaseous nitrous oxide has a density of 1·527, which coincides with that of carbonic anhydride. This gas possesses the qualities neither of an acid nor of an alkali. It supports the combustion of many bodies with a brilliancy resembling that which they exhibit when burned in oxygen. It is, however, at once distinguished from oxygen by its much greater solubility in water. A glowing match bursts into flame when plunged into nitrous oxide: sulphur burns in it with a pale rose-coloured flame. A little nitric oxide is commonly formed during such combustions, and is manifested by the occurrence of ruddy fumes, due to admixture of this gas with the oxygen of the air as it enters the bottle.

Soon after the discovery of nitrous oxide, Davy ascertained

that it may be respired for a few minutes; it then produces a singular species of transient intoxication, attended in many instances with an irresistible propensity to muscular exertion, and often to uncontrollable laughter; hence the gas has acquired the popular name of *laughing-gas*. It is now largely used as an anæsthetic for producing insensibility to pain during surgical operations, especially the extraction of teeth: for this purpose it is condensed in wrought iron bottles in order to facilitate transport.

Composition.—If nitrous oxide be passed repeatedly through a porcelain tube heated to bright redness, the gas is decomposed into a mixture of oxygen and nitrogen, 2 volumes becoming expanded permanently into the space of 3 volumes. An easy method of analysing nitrous oxide consists in mixing it with hydrogen, and passing an electric spark through the mixture. If 4 measures of nitrous oxide be mixed with an excess of hydrogen gas, say with 6 measures of hydrogen, in the bent eudiometer (fig. 287), 10 measures of mixed gas will be produced; and on passing the electric spark, steam will be formed by the oxidation of the hydrogen, and will be immediately condensed, whilst the 10 measures will become reduced to 6: but the quantity of oxygen contained in the nitrous oxide cannot be at once inferred from this change of bulk: before this can be done, it is needful to ascertain how much hydrogen is left in the mixture. This may be effected by mixing the 6 remaining measures with 2 measures of oxygen, thus making 8 measures, and again passing the electric spark. Steam will again be formed, and immediately condensed: the 8 measures of the mixture will now be reduced to 5; 3 measures of the gas will therefore have disappeared, two-thirds of which, or 2 measures, are hydrogen: 1 measure of the gas now left must consequently be oxygen which was added in excess, and the remaining 4 measures are nitrogen. Of the 6 measures of hydrogen originally added, 4 have therefore combined with oxygen derived from the nitrous oxide; and since 4 measures of hydrogen require 2 measures of oxygen for conversion into water, the 4 measures of nitrous oxide must have contained 2 measures of oxygen. It appears, also, that nitrous oxide contains its own bulk of nitrogen, since the 4 measures of the gas originally employed furnish 4 measures of nitrogen; this nitrogen is moreover so combined with 2 measures of oxygen, that the 6 measures of the two gases when united are condensed into the space of 4 measures, or into two-thirds of the bulk which they occupied when separate.

The composition is therefore:

		By weight.	By vol.
Nitrogen	$N_2 = 28$	or 63·64 ...	2·0
Oxygen	$O = 16$	36·36 ...	1·0
Nitrous oxide	$N_2O = 44$	100·00 ...	2·0

The specific gravity of the gas found by experiment, 22·066 hydrogen being 1 (or 1·527 referred to air) confirms this determination of its composition. Hydrogen being taken as the standard

2 vols. of nitrogen weigh	28
1 vol. of oxygen weighs	16
2 vols. of nitrous oxide weigh	44

consequently 1 volume would weigh 22, a number very close to that found by experiment.

The proportion of nitrogen contained in the gas may also be ascertained by means of potassium; for if potassium be heated in nitrous oxide, it burns vividly, and is converted into potassic oxide, leaving a volume of nitrogen equal to that of the gas employed.

(404) **Hyponitrites**, *or Salts of Nitrogen Monoxide.*—By the action of sodium amalgam on a solution of an alkaline nitrate, it is speedily reduced to the nitrite, which, in its turn, undergoes further reduction, yielding amongst other products, sodium hyponitrite, NONa, a salt of which nitrous oxide appears to be the anhydride. On rendering the solution slightly acid with acetic acid, and adding argentic nitrate, the silver salt, NOAg, is obtained as a yellow pulverulent precipitate insoluble in water, and almost insoluble in acetic acid. A solution of sodic hyponitrite is alkaline to test paper, and when strongly acidified with acetic acid and heated, evolves nitrous oxide (Divers, *Proc. Roy. Soc.*, 1871, xix. 425; Zorn, *Deut. chem. Ges. Ber.*, x. 1306).

(405) **NITRIC OXIDE**; *Nitrosyl; formerly Deutoxide*, or *Binoxide, of Nitrogen*, NO = 30* $\left[\begin{matrix}\mathbf{NO}\\\mathbf{NO}\end{matrix}\right]$ *Density* 1·039; *Atomic Vol.* [ ]; *Rel. wt.* 15.—*Preparation.*—1. If nitric acid be diluted with twice its bulk of water, so as to reduce it to a density of about 1·2, and be poured upon copper clippings or metallic mercury contained in a retort, a brisk action speedily occurs; a gentle heat being applied, if necessary, until it commences; the retort becomes filled with red fumes, and a gas is disengaged, which if collected over water will be found to be colourless; 1 ounce, or 30 grams of copper, by solution in about 120 c. c. of

* The vapour density of this compound is anomalous, NO yielding 2 volumes (H = 1 vol.) instead of N_2O_2 as would be requisite if the compound followed the usual law. It is possible that at a sufficiently low temperature its density would become normal, as is the case with nitric peroxide.

the diluted acid would yield nearly 420 cubic inches, or about 7 litres of nitric oxide. If the heat be too high the gas is apt to be contaminated with nitrogen. During this decomposition the metal may be regarded as displacing hydrogen from one portion of the acid to form a nitrate which is dissolved, whilst the hydrogen, at the moment of its liberation, decomposes another portion of the acid, forming water and setting nitric oxide at liberty. The following equation shows the reaction which occurs between 3 atoms of copper and 8 molecules of nitric acid, resulting in the formation of nitric oxide, 3 molecules of cupric nitrate, and 4 of water:

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Cupric nitrate.}}{3(Cu_2NO_3)} + \underset{\text{Water.}}{4OH_2}.$$

$$3Cu + 8NO_2(OH) = \begin{Bmatrix} NO \\ NO \end{Bmatrix} + 3\begin{matrix} NO_2 \\ NO_2 \end{matrix}(O_2Cu)'' + 4OH_2.$$

In the above reaction arsenious anhydride in small lumps may be substituted for the metallic copper, as when heated with nitric acid of density 1·2 it gives off scarcely anything but nitric oxide. The higher oxides of nitrogen may be readily removed by washing with water, or what is more convenient in some cases, by passing the gas through concentrated sulphuric acid.

3.—Nitric oxide gas may also be obtained perfectly pure by digesting hydrochloric acid with iron filings until it will dissolve no more, decanting the clear liquid, and adding to it its own bulk of hydrochloric acid: on placing the solution in a retort, and adding potassic nitrate, nitric oxide is immediately evolved in large quantity (Pelouze). The reaction is not so simple as in the preceding case; it may be represented as follows:

$$\underset{\substack{\text{Ferrous}\\\text{chloride.}}}{6FeCl_2} + \underset{\substack{\text{Hydrochlor.}\\\text{acid.}}}{8HCl} + \underset{\substack{\text{Potassic}\\\text{nitrate}}}{2KNO_3} = \underset{\substack{\text{Nitric}\\\text{oxide.}}}{2NO} + \underset{\substack{\text{Ferric}\\\text{chloride}}}{3Fe_2Cl_6} + \underset{\text{Water.}}{4OH_2} + \underset{\substack{\text{Potassic}\\\text{chloride.}}}{2KCl}.$$

A simple modification of this method consists in placing in a retort 30 grams of commercial nitre, 240 of ferrous sulphate, and pouring upon them 250 cubic centim. of dilute sulphuric acid (1 measure of acid to 3 measures of water). Such a mixture will give about 7 litres of pure nitric oxide.

Composition.—The composition of nitric oxide cannot be ascertained by detonation with hydrogen; for equal volumes of hydrogen and nitric oxide burn quietly with a green flame on the approach of a burning body. Davy analysed nitric oxide by heating charcoal strongly in it; 2 volumes of the gas by this treatment furnish 1 volume of nitrogen, and 1 volume of carbonic anhydride; but carbonic anhydride contains its own

volume of oxygen; nitric oxide must therefore have consisted of 1 volume of nitrogen united without condensation with 1 volume of oxygen.

		By weight.	By vol.
Nitrogen	N = 14	or 46·67 ...	1 vol.
Oxygen	O = 16	53·33 ...	1 vol.
Nitric oxide	NO = 30	100·00 ...	2 vols.

The specific gravity accords with the determination that the gases unite without condensation.

Relative weight of 1 vol. of Nitrogen ...	= 14
„ 1 „ Oxygen ...	= 16
„ 2 vols. of Nitric oxide...	30

The relative weight of one volume of the compound should therefore be 15, whilst experiment gives 15·014 (1·039, air being taken as unity).

Potassium burns when heated in the gas, potassic oxide being produced. If the experiment be conducted in such a manner as to allow the residual gas to be measured after the combustion is over, 2 volumes of nitric oxide will be found to leave 1 volume of nitrogen. A similar result is obtained when tin is heated in the gas.

Properties.—Nitric oxide has a strong disagreeable odour, and cannot be respired. Until recently, it had resisted all attempts to liquefy it, but Cailletet (*Compt. Rend.*, 1877, lxxxv. 1017) has found that at −11° (12°·2 F.), under a pressure of 104 atmospheres, it may be easily condensed; at 8° (46°·4 F.), however, it does not liquefy even under a pressure of 270 atmospheres, so that the critical point appears to lie between these two temperatures. Water does not dissolve more than one-twentieth of its bulk of this gas. Nitric oxide is the most stable of the oxides of nitrogen; it may even be exposed to a red heat without undergoing decomposition, but a succession of electric sparks converts it, if it be moist, into a mixture of nitrogen and nitric acid: and in contact with moistened iron filings, or a moist sulphide of one of the alkali-metals, it is slowly converted into nitrous oxide. Many burning bodies, such, for instance, as a lighted taper, or phosphorus just kindled, are extinguished when plunged into the gas; but if the phosphorus be burning vigorously the temperature will be sufficiently high to enable it to decompose the gas and it will then deflagrate with a brilliancy equal to that produced by its combustion in oxygen. If a thin bulb containing a few drops of carbonic bisulphide be placed in a jar of nitric oxide, closed

by a glass plate, and agitated briskly, so as to break the bulb and diffuse the vapour through the gas, a mixture will be obtained which on the approach of a flame burns with an intense whitish blue light.

Nitric oxide is completely absorbed by a solution of ferrous sulphate, forming a deep reddish-brown liquid. All the ferrous salts exert a similar action, and, according to Péligot, 4 molecules of the salt of iron absorb 1 molecule of nitric oxide, the solution in the case of the sulphate containing, $4FeSO_4.N_2O_2$. This property, as has been already mentioned (402), is employed for the purpose of detecting the presence of nitric acid in solution. This liquid absorbs oxygen rapidly from the air or from gaseous mixtures; when heated, most of the nitric oxide is expelled from it unchanged, affording a ready means of obtaining the gas in a pure state. Solutions of stannous and mercurous salts also absorb nitric oxide, but they undergo change, and the gas cannot again be expelled from them by heat. Nitric acid likewise absorbs the gas rapidly; if the acid be concentrated, the solution becomes reddish-brown; if more dilute it is green; if still weaker, the solution is blue, but if diluted below a density of 1·15, little of the gas is absorbed, and the acid remains colourless.

Nitric oxide is neither acid nor alkaline in its characters. It has, however, a very powerful attraction for oxygen, and to this circumstance one of the most characteristic properties of the gas is due: when mixed with oxygen, or with any gas containing uncombined oxygen, dense red fumes are formed, which are freely soluble in water, producing an acid liquid. Formerly this circumstance was employed to determine the quantity of oxygen in gaseous mixtures; but the method is now abandoned, as the absorption is not uniform, owing to the formation in uncertain quantity of a mixture of the soluble oxides of nitrogen. It may, however, be used with advantage as a qualitative test to demonstrate the existence of uncombined oxygen in a gaseous mixture. Nitric oxide also unites with half its volume of chlorine when the two gases are mixed, and nitrous oxychloride or nitrosyl chloride, NOCl, is formed (410).

(406) **NITROUS ANHYDRIDE**: $N_2O_3 = 76$ $\left[\begin{matrix}\mathbf{NO}\\ O\\ \mathbf{NO}\end{matrix}\right]$.—*Preparation.*—1. By mixing in an exhausted flask 4 volumes of nitric oxide with 1 volume of oxygen, both in a perfectly dry state, brownish-red fumes of nitrous anhydride are formed, which at a

temperature of $-18°$ (0°·4 F.) become condensed into a very volatile blue liquid, which emits a red vapour.

2.—Nitrous anhydride may also be obtained in an impure state, by heating in a capacious retort 1 part of starch with 8 parts of nitric acid of density 1·25: it can be dried by means of calcic chloride, and may then be liquefied by passing it through a U-shaped tube surrounded by a mixture of ice and salt.

3.—By passing a mixture of nitric dioxide and tetroxide (or the gases evolved on heating arsenious anhydride in lumps, at 70° (158° F.), with nitric acid of density 1·3,) through a red-hot tube, nearly pure nitrous anhydride is obtained. This may be condensed by means of a freezing mixture to a liquid which is dark blue at the ordinary temperature, and indigo blue at $-10°$ (14° F.). According to Streiff, it may also be obtained by adding water gradually to nitrosyl sulphate, $H.NO.SO_4$, when the anhydride is given off in the gaseous state.

Properties.—Nitrous anhydride cannot be distilled unchanged under the ordinary atmospheric pressure. A small quantity of water converts the anhydride into nitrous acid, but a larger quantity quickly decomposes it into nitric acid and nitric oxide: hence the presence of a small quantity of water converts the blue into a dark green liquid, but a larger quantity decomposes it with effervescence: nitric acid is formed and nitric oxide escapes. This last reaction may be thus represented: $OH_2+3N_2O_3$ give $2HNO_3+4NO$. Nitrous anhydride dissolves in a very large quantity of water, yielding a solution of nitrous acid, HNO_2.

Nitrites.—The salts which nitrous acid forms when its hydrogen is replaced by a metal have the general formula $M'NO_2$, and are called *nitrites*. If nitric oxide be placed over a solution of potassic hydrate, and small quantities of oxygen be added, potassic nitrite is produced in the liquid; and if nitre, or sodic nitrate, be heated to redness until the gas which is evolved begins to contain nitrogen, the residue will be found to be composed chiefly of potassic or sodic nitrite. These nitrites are soluble in alcohol, and may thus be separated from the corresponding nitrates, which are insoluble. The normal nitrites of sodium, silver, and lead are anhydrous. A considerable number of double nitrites of potassium may be formed. Lang has, for instance, among others, described the following:

Nitrite of potassium		$2KNO_2.OH_2$
„ „	and barium ...	$2KNO_2.Ba2NO_2.OH_2$
„ „	and zinc	$2KNO_2.Zn2NO_2.OH_2$
„ „	barium and nickel...	$2KNO_2.Ba2NO_2.Ni2NO_2$.

If the nitrite either of potassium or of sodium be dissolved in water, and argentic nitrate be added, a sparingly soluble argentic nitrite is precipitated, which may be purified by crystallization from hot water. The addition of cold dilute sulphuric acid to a solution of a nitrite decomposes the salt, and the liquid then becomes of a brownish-red colour on adding a solution of ferrous sulphate. The nitrites may thus be distinguished from the nitrates, since the latter do not change colour when similarly treated, unless concentrated acid be employed. A very minute trace of any nitrite may be detected by mixing a dilute solution of potassic iodide, free from iodate, with starch and a little dilute hydrochloric acid (density 1·006); the liquid to be tested, after being acidulated with hydrochloric acid, is then to be added to the test mixture, when the blue colour of iodide of starch will appear, if any trace of a nitrite be present. Acid solutions of the nitrites destroy the blue colour of indigo at ordinary temperatures, acting in this as in the preceding cases by its oxidizing powers; but in other instances it shows reducing powers equally marked. Acidulated solutions of the nitrites, for example, bleach potassic permanganate, and slowly reduce potassic chromate to a green salt of chromium. Auric chloride is reduced to metallic gold by these salts, and mercurous salts give a grey precipitate of reduced mercury.

The presence of nitrites in the well waters of towns is of common occurrence, probably owing to the oxidation of ammonia or of nitrogenous organic matter. Ammonia becomes oxidized to nitrous acid when it is in contact with atmospheric air in the presence of platinum black, or of a coil of heated platinum wire; if a coil of red-hot platinum wire be held in a jar of air whose sides are wetted with a few drops of a strong solution of ammonia, white fumes of ammonic nitrite will be formed. The contact of metallic copper is still more effectual in promoting the formation of nitrous acid from ammonia, when free oxygen is present; if a small quantity of finely divided metallic copper be shaken up with a few drops of a solution of ammonia in a bottle containing air, the oxygen will be absorbed in a few minutes, and nitrous acid will be found in the liquid. Even bright slips of copper effect a similar oxidation of the ammonia, oxide of copper being simultaneously formed. The cause of these phenomena is obscure. According to Schönbein, the white fumes produced during the spontaneous oxidation of phosphorus in air consist, not of phosphorous anhydride, but of ammonic nitrite formed by the action of the ozone upon moist air.

Schönbein has shown that the solutions of the nitrates of the alkali-metals, as well as some other nitrates, may be reduced slowly to nitrites by stirring or agitation with a rod of zinc or of cadmium, the reduction being accelerated by heat.

(407) **PEROXIDE OF NITROGEN**; *Nitric peroxide,* or *Hyponitric acid,* $N_2O_4=92$, or $NO_2=46$ $\left[\begin{matrix}NO_2\\NO_2\end{matrix}\right]$; *Melting-pt.* $-10°$ (14° F.), Deville and Troost; *Boiling-pt.* 22° (71°·6 F.).—*Preparation.*—1. The red fumes which appear on mixing nitric oxide with atmospheric air consist mainly of peroxide of nitrogen. The peroxide may be procured in prismatic crystals by passing two volumes of nitric oxide and one of oxygen, both perfectly dry, into tubes previously dried with scrupulous care, and cooled down by a mixture of ice and salt (Péligot, *Ann. Chim. Phys.*, 1841, [3], ii. 61). These crystals melt at $-10°$ (14° F.); at the ordinary temperature of the air they form an orange-coloured liquid, which boils at 22° (71°·6 F.), and produces a deep brownish-red vapour. It is remarkable that after this compound has once been melted, it does not freeze even at $-21°·3$ ($-6°·3$ F.). This substance is decomposed by water with singular facility; a minute trace of water is sufficient to prevent the formation of the crystalline compound, occasioning in its stead the production of a green liquid (probably $N_2O_3.N_2O_5.OH_2$), similar to that obtained by the distillation of plumbic nitrate. The peroxide of nitrogen was long considered to possess the properties of an anhydride, and hence was termed hyponitric acid. It, however, does not form specific salts, but is immediately decomposed by bases into a nitrate and nitrite:

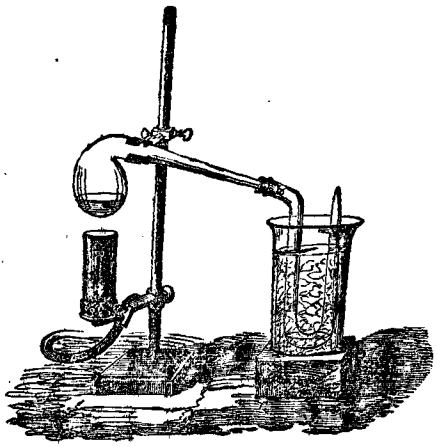
$$N_2O_4+2KHO, \text{ yielding } KNO_3+KNO_2+OH_2.$$

But when the liquid peroxide is digested with a metal, such as potassium, lead, or mercury, nitrate of the metal is formed, and nitric oxide is expelled; with potassium, for instance, the reaction is as follows: $K+N_2O_4=KNO_3+NO$. No nitrite is formed under these circumstances.

2.—If dry plumbic nitrate, $Pb2NO_3$, be heated strongly in a small glass retort, it is decomposed; deep red fumes, consisting of a mixture of peroxide of nitrogen and free oxygen are produced, and plumbic oxide is left: $2(Pb2NO_3)=2PbO+2N_2O_4+O_2$. If the red vapour be made to pass through a bent tube surrounded by ice and salt, as shown in fig. 315, the peroxide is condensed

to a liquid which is green, owing to the presence of a little moisture. Towards the latter part of the distillation the anhydrous peroxide comes over, and if the receiver be changed, it may be obtained in crystals. The melted peroxide is nearly colourless at $-18°$ (0° F.): it becomes yellow at $-10°$ (14° F.), and at ordinary temperatures is red. It has a density of 1·451, boils at 22° (71°·6 F.); (28° C., or 82° F.; Müller), and freezes at $-40°$ ($-40°$ F.). It emits a dense brownish-red vapour, which becomes deeper in tint as the temperature rises, until at 38° (100°·4 F.), it is almost opaque.

Fig. 315.



3.—The peroxide may also be obtained by acting on arsenious anhydride with nitric acid of density about 1·39, condensing the mixture of nitrous anhydride and nitric peroxide, which are evolved in the gaseous state, and passing a current of air or oxygen through the liquid to convert the nitrous anhydride into peroxide. It may then be rectified (Hassenbach, *Jour. pr. Chem.*, 1871, [2], iv. 1).

Playfair and Wanklyn have shown it to be probable that at low temperatures the compound has the formula N_2O_4, but that as the temperature rises it assumes the constitution NO_2. Müller (*Ann. Chem. Pharm.*, 1862, cxxii. 15) finds the density of the vapour, at 28° (82°·4 F.) to be 2·70; N_2O_4=[ ] theoretically would give 3·18; whilst at 77° (170°·6 F.) the density of the vapour is only 1·84; and Mitscherlich, at some temperature not stated, but probably higher, found it as low as 1·71. Deville and Troost (*Compt. Rend.*, 1867, lxiv. 257) found the specific gravity to be 2·65 at 26°·7 C.; 2·08 at 60°·2; 1·8 at 80°·6; 1·68 at 100°·1; 1·58 at 154°; and 1·57 at 183°·2, showing that at temperatures above 154° the N_2O_4 is entirely dissociated into NO_2. The result of these experiments gives 1·589 as the vapour density of nitric peroxide at temperatures above 154°, whilst the calculated density for the formula NO_2=[ ] is 1·591.

The molecule of nitric peroxide is, therefore, differently constituted at different temperatures; at low temperatures its composition is

				By weight.	By vol.
Nitrogen	N_2	=	28 or 30·44	...	2
Oxygen	O_4	=	64 69·56	...	4
			92 100·00	...	2

And the relative weight would be 46, or one-half the molecular weight: experiment gives 38·294 at 26°·7 (80°·1 F.).

At higher temperatures it consists of:

				By weight.	By vol.
Nitrogen	N	=	14 or 30·44	...	1
Oxygen	O_2	=	32 69·56	...	2
			46 100·00	...	2

The relative weight being 23, the experimental number being 22·740 at 183°·2 (361°·76 F.).

This vapour has a peculiar, suffocating odour. It supports the combustion of a taper, and of many burning bodies; potassium takes fire in it spontaneously. If water be added gradually to the liquid peroxide, it passes through various tints, becoming successively orange, yellow, green, blue, and finally colourless, an effervescence being occasioned during the whole time from the escape of nitric oxide; finally, nitric acid in abundance is formed in the liquid; $OH_2 + 3NO_2 = NO + 2HNO_3$. The nitric oxide, on mixing with the oxygen of the air, reproduces the peroxide of nitrogen as usual. The different tints assumed by the liquid during dilution appear to be owing to the solution of the nitric oxide in varying proportion in the nitric acid produced by the decomposition. Peroxide of nitrogen combines directly with hydrochloric acid, and forms several chlorinated compounds. It is also absorbed by concentrated sulphuric acid, and forms a crystalline compound with it, $2H_2SO_4.N_2O_4SO_3$; (*note*, p. 210).

Peroxide of nitrogen may be distinguished from nitrous acid by its power of imparting to a neutral solution of potassic sulphocyanide a red tint closely resembling that produced in the same reagent by ferric salts; in a few minutes, however, the decomposition proceeds further, and the liquid becomes colourless.

The important influence of proportion upon the products of chemical combination is exhibited in a striking light by these compounds of nitrogen with oxygen. The same elements, according to the quantities in which they are united, may, as in nitric anhydride, produce a substance which when united with the elements of water forms one of the most corrosive compounds

in the range of chemistry; or may give rise, as in the case of nitrous oxide, to a stimulating and intoxicating gas, which may be breathed with impunity; whilst the intermediate combinations exhibit properties entirely different from either. A broad distinction may also be easily traced between the results of mixture and those of true chemical union. The properties of the atmosphere are the result of simple admixture: the chemical qualities of oxygen appearing to be rendered less energetic by its apparently inert companion, nitrogen (just as the sweetness of sugar is reduced by the addition of water); whilst each one of the true combinations of nitrogen with oxygen exhibits characters distinct from those of either of its components.

(408) **NITRYLIC CHLORIDE**, or *Chloride of Nitryl*, $NO_2Cl = 81{\cdot}5$; *density of liquid*, 1·32; *of vapour*, 2·63; *theoretic density of vapour*, 2·8199; *rel. wt.* 40·75. It is usually stated that this compound may be prepared by the action of phosphoric oxytrichloride on plumbic or argentic nitrate, in the manner represented in the following equation:

$3AgNO_3$	+	PCl_3O	=	Ag_3PO_4	+	$3NO_2Cl$
Argentic nitrate.		Phosphoric oxytrichloride.		Argentic phosphate.		Nitrylic chloride.
$[3NO_2(OAg)$	+	$POCl_3$	=	$PO(OAg)_3$	+	$3NO_2Cl.]$

Mills finds, however, that the reaction does not take place in the manner indicated.

Nitrylic chloride may be obtained by the action of chlorhydrosulphuric acid on potassic nitrate:

KNO_3	+	$HClSO_3$	=	$KHSO_4$	+	NO_2Cl
Potassic nitrate.		Chlorhydrosulphuric acid.		Hydric potassic sulphate.		Nitrylic chloride.
$[NO_2(OK)$	+	$SO_2Cl(OH)$	=	$SO_2(OH)(OK)$	+	$NO_2Cl.]$

Also by passing a mixture of chlorine and nitric peroxide through a heated tube, $NO_2 + Cl = NO_2Cl$. *Nitrylic bromide*, NO_2Br, may be prepared in the same way.

Nitrylic chloride appears to be produced, together with other compounds, by the action of dry hydrochloric acid on dry nitric peroxide.

Nitrylic chloride is a liquid of a pale yellow colour which boils at 5° (41° F.), and does not solidify at −31° (−23°·8 F.); by the action of water it is decomposed into hydrochloric and nitric acids.

NO_2Cl	+	OH_2	=	HCl	+	HNO_3
Nitrylic chloride.		Water.		Hydrochloric acid.		Nitric acid.
$[NO_2Cl$	+	OH_2	=	HCl	+	$NO_2(OH)].$

(409) **AQUA REGIA**: *Nitro-muriatic Acid.*—The name of *aqua regia* was given by the alchemists to a mixture of nitric and hydrochloric acid, from the power that it possesses of dissolving gold, the "King of Metals." Both platinum and gold are insoluble in either acid separately, but when the two acids are mixed, they decompose each other; free chlorine, and abundant ruddy fumes, long mistaken for peroxide of nitrogen, being liberated; the chlorine in the nascent state acts upon the metals

and dissolves them. The red gas with which the chlorine is mixed consists of nitrosyl chloride.

Aqua regia is largely employed as an oxidizing agent; by its action, perchlorides of the metals are formed in solution, and when the liquid is decomposed by an alkali, the oxide of the metal corresponding in composition to its perchloride is precipitated. By boiling the solutions of the metals in aqua regia, with excess of hydrochloric acid, the whole of the nitric acid may be decomposed and expelled, and a pure solution of the metallic chlorides with excess of hydrochloric acid will be formed.

(410) **NITROSYL CHLORIDE,** *Nitrous oxychloride* or *chloronitrous gas*, NOCl; [NOCl]; *Theoretic density* 2·2663, *observed* 2·29 (Tilden); *Molecular Vol.* [ ]; *Rel. wt.* 32·75.—If a mixture of 1 part of concentrated nitric acid (density 1·42) and 4 parts of hydrochloric acid (density 1·16) be placed in a flask and subjected to a gentle heat in the water bath, red fumes pass off in abundance. These vapours, if passed through a bottle cooled by immersion in melting ice, deposit a little volatilized hydrochloric acid and water, but the red fumes pass on, and may be condensed as a heavy red liquid in a tube receiver surrounded by a mixture of ice and salt, whilst free chlorine escapes from the open extremity of the tube. This red liquid which Gay-Lussac (*Ann. Chim. Phys.*, 1848, [3], xxiii. 203) supposed to be a nitric oxydichloride, $NOCl_2$, has since been proved by Tilden (*Jour. Chem. Soc.*, 1874, xxvii. 630) to be merely a solution of chlorine in nitrosyl chloride in variable proportion.

Nitrosyl chloride may be obtained in a pure state by gently heating a mixture of nitrosyl sulphate, $H.NO.SO_4$, (lead chamber crystals) with sodic chloride, and passing the orange-coloured gas which is evolved through a tube cooled by a freezing mixture. The gas cannot be collected over mercury, for it is immediately decomposed with formation of mercurous chloride and nitric oxide: $2NOCl + 2Hg = Hg_2Cl_2 + N_2O_2$. When chlorine is mixed with nitric oxide in the gaseous state, they combine, and yield a dense orange-coloured gas: 2 volumes of nitric oxide and one of chlorine producing 2 volumes of nitrosyl chloride. At low temperatures nitrosyl chloride condenses to a deep orange-coloured limpid liquid which boils at $-8°$ (17°·6 F.) without decomposition.

In the early stages of the decomposition of aqua regia, the product contains a large excess of chlorine, but as the decomposition advances the proportion of nitrous oxychloride NOCl increases. Nitrosyl chloride attacks platinum and gold very slowly, but the action is much more rapid with Gay-Lussac's supposed dichloride, the metal in both cases being ultimately converted into a yellow crystalline powder. These compounds are decomposed by water, with escape of nitric oxide, yielding a solution of the metallic chloride.

According to Geuther (*Jour. pr. Chem.*, 1873, [2], viii. 854) nitric peroxide acts on boric trichloride, giving rise to boric anhydride and a compound BCl_3NOCl which crystallizes in rhombic prisms: these melt and decompose at about 23° (73°·4 F.). Water acts violently on them, yielding boric acid, chlorine, and nitrous acid.

(411) **BORIC NITRIDE,** or **NITRIDE OF BORON:** BN.—As already mentioned, boron combines with nitrogen at a red heat with great avidity. Boric nitride may also be obtained by passing a current of dry nitrogen gas over a mixture of 1 part of pure finely-powdered charcoal, with 4 parts of fused boracic anhydride, exposed to a full white heat in a porcelain tube. It

may likewise be procured readily by mixing 1 part of anhydrous borax with 2 parts of ammonic chloride, and heating it to full redness in a covered platinum crucible; a white, infusible, porous mass is left, which, when boiled with dilute hydrochloric acid and well washed, yields boric nitride as a white, light, amorphous, insoluble powder, which feels like talc when rubbed upon the skin. It may be heated in hydrogen or in chlorine without change; it is but very slowly acted upon by concentrated acid or alkaline solutions; but when fused with potassic hydrate it is converted into ammonia and potassic borate, $3KHO + BN = KBO_2 + K_2O + NH_3$. In a current of steam it is completely converted into ammonic borate: $BN + 2OH_2 = NH_4BO_2$. It is also decomposed when heated with easily reducible metallic oxides, such as those of lead or copper, nitric oxide being evolved.

CHAPTER XI.

SULPHUR: s = 32.

Combining Volume below 816° (1500° F.) $\frac{1}{8}$; *above* 1040° (1904° F.) $\square$; *Rel. wt.* 32; *Observed Density of Vapour at* 1040° (1904° F.), 2·23; *at* 482° (900° F.), 6·617; *Theoretic Density* 2·2144; *Melting-pt.* 113° (235°·4 F.); *Boiling-pt.* 446° (836° F.); *Dyad, as in* SH_2, *Tetrad in Sulphurous Anhydride* $[S^{iv}O_2]$, *and in Triethyl-sulphine Iodide* $[S^{iv}(C_2H_5)_3I]$, *and Hexad in Sulphuric Acid* $[S^{vi}O_2(OH)_2]$, *and in Sulphuric Dioxydichloride* $[S^{vi}O_2Cl_2]$; *Mol. vol. of Vapour* (SS)=$\square\square$; *Mol. wt.*=64.

(412) This element is the representative of the hexad non-metallic elements. Most of the sulphur used in England is obtained from Sicily, where it occurs in the native or uncombined state in beds of a blue clay formation, stretching from the southern coast of the island towards the base of Mount Etna. It is also found abundantly in most volcanic districts, and particularly in those which border the Mediterranean. Many of the compounds of sulphur with the metals occur in great abundance as natural productions,—especially the sulphides of iron, copper, lead, and zinc. Ferric disulphide, FeS_2 (iron pyrites) furnishes a large proportion of the sulphur consumed in the manufacture of oil of vitriol, enormous quantities being imported from Spain and Portugal for that purpose. Sulphur is still more extensively distributed in the oxidized condition in the form of sulphates; the sulphates of calcium, magnesium, barium, and strontium being abundant natural productions. Sulphur is likewise an essential constituent of many bodies of organic origin; it enters into the composition of several

fœtid volatile oils; it is a necessary ingredient in the muscular tissue of animals, and is indeed always contained in the albuminoid or proteid compounds.

Properties.—Native sulphur is found either in amorphous masses, or in transparent yellow crystals, the form of which is derived from the octohedron with a rhombic base. Sulphur occurs in commerce, either as a harsh, yellow, gritty powder, known as *flowers of sulphur*, or in round sticks, constituting roll sulphur or common *brimstone*. In the latter condition it is a solid, translucent, brittle substance, of a characteristic yellow colour, with a slight, peculiar odour. It is insoluble in water, and is consequently tasteless; it is a bad conductor of heat, and when grasped with a warm hand frequently crackles and falls to pieces from the unequal expansion; it is an insulator of electricity, and becomes negatively electric by friction.

Sulphur is highly inflammable, and when heated in the air, it takes fire at between 235° and 260° (455° and 500° F.) and burns with a blue flame, emitting pungent suffocating fumes of sulphurous anhydride. Pollacci (*Gazzetta Chimica Italiana*, v. 237) has shown that sulphur in a finely divided state becomes oxidized to sulphuric acid on exposure to the air even at the ordinary temperature. This action takes place slowly below 35° (95° F.), but rapidly at 65° (149° F.). At 113°—113°·5 (235°·4—236°·3 F., Pisati), sulphur melts, forming a yellow liquid which is less dense than the unmelted sulphur, and at a higher temperature it may be distilled, the boiling point being about 446° (836° F.) (Regnault); at this temperature sulphur yields a deep yellow vapour of density 6·617, 1 volume of which contains 3 atoms of sulphur. Bineau found that when sulphur is heated to about 1000° (1832° F.), the vapour becomes dilated to three times the bulk that an equal weight of the vapour occupies at 482° (900° F.), and that at this high temperature the volume occupied by an atom of sulphur vapour corresponds with that of an atom of oxygen; this observation has recently been confirmed by Deville and Debray.

Sulphur combines readily with chlorine, with bromine, and with iodine, especially when the action is favoured by heat. It also enters rapidly into combination with most of the metals, many of which, like copper, iron, and silver, if in a state of fine division, burn vividly when heated in its vapour. The compounds of sulphur with the metals are now usually termed *sulphides*; but they were formerly known as *sulphurets*. Generally a sulphide exists corresponding to each oxide, each atom of oxygen in

the molecule of the oxide being replaced in the sulphide by an atom of sulphur; and sulphur often displaces oxygen by double decomposition; 1 atom of sulphur is therefore equivalent to 1 atom of oxygen and consequently to 2 atoms of hydrogen or of chlorine.

Extraction.—When the proportion of sulphur in the matrix is large, the earthy impurities are removed by simply melting out the sulphur from them; but when the proportion of sulphur does not exceed 8 to 12 per cent., it is found to be more advantageous to subject the mineral to a rough distillation, performed upon the spot where it is obtained. For this purpose a long brick furnace is arranged so as to contain a double row of upright earthenware retorts, each of a capacity of 4 or 5 gallons (18 or 22 litres): the retorts are furnished with a large aperture at the top for charging them with the crude sulphur, and with a short wide tube, which proceeds from the side at the upper part, and slopes downwards through the walls of the furnace into an earthen receiver of a form similar to that of the retort: from the bottom of the receiver a short pipe carries off the melted sulphur into a vessel containing water. It is, however, still very impure, and requires rectification before it is fit for many of the purposes to which it is applied in the arts. This second distillation is conducted in retorts, generally of iron, furnished with a short wide, lateral neck; the fumes are received into large chambers of brickwork. If the walls of these chambers be kept cool, and the process be conducted slowly, the sulphur is condensed in powder, and forms 'flowers of sulphur'; but if the fire be urged, and the masonry be allowed to become hot, the sulphur melts, runs down, and is then drawn off into cylindrical wooden moulds, in which it is cast into the usual form of roll sulphur. A detailed account of the method of extracting sulphur employed in Sicily and written by Barbaglia will be found in Hofmann's 'Bericht über die Entwickelung der chemischen Industrie während des letzten Jahrzehends,' i. 144.

When sulphur is prepared from pyrites, FeS_2, the mineral is sometimes distilled in closed vessels, and by this means about one-third of the sulphur which it contains is volatilized and condensed, magnetic pyrites, Fe_3S_4, remaining; but it is more usual to conduct the operation in the open air, as a preliminary step in the roasting of copper pyrites to prepare it for smelting. Huge heaps of the ore are arranged in the form of a truncated square pyramid, the base of which is about 30 feet (or 10 metres) in the side. A layer of powdered ore is placed at the bottom, and over this one of brushwood; in the centre is constructed a wooden chimney, which communicates with air-ways left between the fagots; fragments of ore are now piled up until the heap is about 8 feet (2·5 metres) high, and lastly the whole is covered, for a depth of 12 inches (30 centimetres), with a layer of powdered ore. Such a heap contains upwards of 2000 tons of pyrites, and will furnish about 20 tons of sulphur. When the construction of the heap is complete, the fire is kindled in the centre by dropping lighted fagots down the chimney; in the course of a few days the heat becomes diffused throughout the mass, and sulphur begins to ooze from the surface. When this is observed, numerous hemispherical wells or excavations, fitted with covers, are made in the superficial layer of ore, for the reception of the sulphur; into these cavities it drains, and is daily ladled out and cast into moulds. The process of roasting such a heap occupies five or six months. The operation is also frequently conducted in kilns somewhat resembling lime-kilns, but connected with suitable condensing chambers, the pyrites being supplied continuously at the top, and the burnt ore removed below. In this way the heat developed by

the burning of part of the sulphur to sulphurous anhydride, and the oxidation of the iron, is sufficient to volatilize the remainder of the sulphur. By this process about one-half of the sulphur in the pyrites is obtained as such.

Uses.—Sulphur is extensively employed in the arts; from its ready inflammability, it is used to facilitate the combustion of many bodies, as in the preparation of matches, although in England it has for this purpose been superseded by paraffin; and large quantities are consumed in the manufacture of gunpowder. It is employed to some extent as a medicine, especially in certain forms of cutaneous disease; and when converted into sulphurous acid it is applied to the bleaching of silks and flannels; its chief consumption, however, is in the production of sulphuric acid.

(413) **Various forms of Sulphur.**—Sulphur has been already pointed out (87) as affording a striking illustration of the occurrence of allotropy; it may be obtained in several distinct modifications of form, or in different allotropic states.

The first form is the native crystal of sulphur, the octohedron with a rhombic base. It may be obtained artificially by allowing the solution of sulphur in chloride of sulphur, or in carbonic bisulphide, to evaporate spontaneously. It is semi-transparent, of an amber yellow colour, and has a density of 2·0748 at 0° (32° F.). Its crystals undergo no change in the air: they fuse at 113° (235°·4 F.).

The second variety is obtained by melting 2 or 3 kilograms of sulphur, and allowing it to solidify on the surface; if the crust be pierced with a hot wire, the still fluid portion may be poured off, and the solid mass beneath will be found to be lined with transparent brownish-yellow needles, belonging to the oblique prismatic form; these have a density considerably less than octohedral sulphur, viz., 1·98, the density of ordinary roll sulphur. According to Brodie, it melts at 120° (248° F.). This form is not permanent in the air: in a few days, or (if the surface of the crystals be scratched) in a few hours, the transparency disappears, and although to the eye the crystals retain their prismatic outline, they lose their coherence, and an opaque crumbling mass is produced, consisting of minute rhombic octohedra. On the other hand, if an octohedron of sulphur be placed in a liquid, the temperature of which is slowly raised to a point between 104° and 110° (220° and 230° F.), it loses its transparency, owing to the formation of prismatic crystals. Gernez has found that if a crystal of octohedral sulphur he gently lowered into a solution prepared by heating octohedral sulphur with toluene at 80°

(176° F.), and allowing it to cool to 15° (59° F.), crystallization commences at once, and the whole of the sulphur is deposited in the octohedral form; whereas, if a prismatic crystal is introduced into the original solution, all the crystals formed are prismatic. Again, if sulphur be melted and allowed to cool, it will remain fluid if carefully protected from dust, although crystallization sets in readily on stirring it, or on the introduction of a fragment of prismatic sulphur; the crystals formed in this case being prismatic. If, however, an octohedral crystal be introduced into the still fluid mass, octohedral crystals only are formed, the solidification taking place much more slowly, and being accompanied by a marked contraction (about one-seventh). The mass of crystals in both cases remains transparent (*Compt. Rend.*, 1874, lxxix. 219; and 1876, lxxxiii. 217).

Mitscherlich has ascertained that in the passage of the prismatic into the octohedral form, an amount of heat is emitted which would raise the temperature of an equal weight of water 2°·27 (4°·09 F.). This conversion of the prismatic into the octohedral variety may be effected suddenly, by immersing the prisms in a solution of carbonic bisulphide, even when this solvent is already saturated with sulphur (*Ann. Chim. Phys.*, 1856 [3], xlvi. 124).

The third variety, which is produced by the action of a still higher temperature, is even more remarkable than the preceding forms. The influence of heat upon sulphur is very peculiar. It begins to melt at about 113° (235°·4 F.), and between 120° (248° F.) and 140° (284° F.), it forms a yellow, transparent, and tolerably limpid liquid; as the temperature rises, the colour deepens, it becomes brown, and at last nearly black and opaque. This change Lockyer finds to be accompanied by a change in the absorption spectrum, the transmitted light containing more red and less blue. At 180° (356° F.) these changes are very decided; it gradually becomes more and more viscid: the temperature at this point for awhile becomes stationary, notwithstanding continued accessions of heat from without, so that heat is becoming absorbed, as in the analogous case of the melting of ice. After awhile, if the application of heat be steadily continued, the temperature again rises, and when it has attained to nearly 260° (500° F.), the sulphur once more liquefies, although it never becomes as fluid as when first melted at the temperature of 120° (248° F.). If it be now suddenly cooled by pouring it in a slender stream into cold water, a soft tenacious mass is produced, which may be drawn out into elastic threads. The colour of the

cooled threads varies from a pale amber to a deep brown, becoming darker in proportion to the elevation of temperature which it has experienced. Magnus has shown (*Pogg. Ann.*, 1854, xcii. 398) that this deepening in colour of the melted sulphur is due to the formation of another modification of sulphur, which is black; the more frequently the sulphur is heated up to about 315° (599° F.), and then suddenly cooled, the larger is the quantity of this black sulphur which is formed: the details of the process required for isolating it are given at length in the memoir above referred to. A red variety of sulphur was also obtained by Magnus, which Mitscherlich proved to be produced only when a minute quantity of some fatty body is present. Ductile sulphur has a density of only 1·957. In a few hours it becomes yellow and opaque, and returns to the brittle form, giving out again the heat which it had absorbed; it also increases in density, the greater part of it assuming the octohedral form. If this ductile sulphur be heated to 100° (212° F.), it suddenly returns to the brittle condition, the temperature rising to 110° (230° F.) during the change.

(414) According to Berthelot (*Ann. Chim. Phys.*, 1857, [3], xlix. 435) there are among the various modifications of which sulphur is susceptible, two principal forms which are more stable than the rest. These are the *octohedral*, or, as he terms it, the *electronegative* variety, the most permanent condition of sulphur, and a pulverulent, or *electropositive* form, which is insoluble in carbonic bisulphide.

In the so-called electronegative or octohedral condition, sulphur is soluble in carbonic bisulphide. This variety is deposited at the positive electrode of the voltaic battery during the electrolysis of an aqueous solution of sulphuretted hydrogen. To this variety, the prismatic form, and the white precipitate obtained from the alkaline polysulphides by the addition of an acid, also belong. It is this form which is always deposited from cold solutions of sulphur; whether the solvent be alcohol, benzene, carbonic bisulphide, or chloride of sulphur.

The electropositive variety is obtained when sulphur is separated from its combinations with elements which, like oxygen, bromine, and chlorine, are more electronegative than sulphur itself. The most stable variety is that obtained by treating flowers of sulphur first with carbonic bisulphide, then with alcohol, and then a second time with the bisulphide: it is somewhat less stable when prepared from the chloride of sulphur by decomposing it with water; if the precipitate thus obtained be purified by digestion in carbonic bisulphide, a yellow, or orange-yellow, amorphous powder is left. This amorphous sulphur is much more readily oxidized by the action of hot nitric acid than the crystalline modification. If maintained at 110° (230° F.) for some time, it gradually passes into the octohedral modification, with simultaneous development of heat. If amorphous sulphur be heated to 300° (572° F.), then suffered to cool very slowly, and submitted to 2 or 3 successive sublimations at a low temperature, it becomes converted into the electronegative condition, and is then entirely

soluble in carbonic bisulphide. The electropositive variety may also be slowly converted into the electronegative form by contact with certain electropositive substances, as by digestion for some days in an aqueous solution of ammonia, in one of disodic sulphide, or in one of hydric potassic sulphite, $KHSO_3$, in which case a portion of the sulphur becomes dissolved, and the remainder is rendered soluble in carbonic bisulphide. Electropositive sulphur is deposited at the negative electrode of the battery during the electrolysis of sulphurous or sulphuric acid. Other modifications of the insoluble form of sulphur, which pass with greater facility than the foregoing one into the soluble variety (for example, by exposure to 100° (212° F.) for some hours), may be obtained by decomposing the oxidized compounds of sulphur, such as the thiosulphates (hyposulphites) by acids. The black sulphur of Magnus is also insoluble in carbonic bisulphide.

Crystalline sulphur, of either the octohedral or the prismatic form, is soluble in about 3 times its weight of carbonic bisulphide at the ordinary temperatures; it is also dissolved freely by chloride of sulphur, and crystallizes out again in octohedra by the spontaneous evaporation of these liquids. Benzene is an excellent solvent for sulphur, especially when heated. Boiling oil of turpentine likewise dissolves sulphur freely, and as the liquid cools, the sulphur crystallizes out first in the prismatic form, afterwards, as the temperature continues to fall, in octohedra; the solution retains 1·5 per cent. of sulphur when cold. Vitreous sulphur is but partially soluble in carbonic bisulphide, and even after it has lost its vitreous and tenacious character by exposure to the air, it is not wholly changed into the crystalline form of sulphur, a pale buff-coloured powder of density 1·955 being left when it is treated with carbonic bisulphide; it may, however, be reconverted by fusion into ordinary sulphur, soluble in carbonic bisulphide. If vitreous sulphur be left in contact for 24 hours with an aqueous solution of sulphuretted hydrogen, it is changed into the amorphous form.

All the varieties of sulphur are soluble to a small extent in boiling anhydrous alcohol, the electropositive varieties becoming modified as they are dissolved: the hot solution as it cools deposits minute transparent prismatic crystals of the electronegative variety. Chloroform and ether dissolve sulphur less freely than alcohol.

When sulphur is distilled in small quantities, and received into vessels in which the temperature is not considerably reduced, the sulphur is condensed in red drops, which remain liquid for many hours. Sulphur is also frequently liberated in the ductile form from the native sulphides of the metals during their solution in *aqua regia*, and from the thiosulphates (hyposulphites) when decomposed by concentrated hydrochloric acid. When nitric acid is used, the sulphur is separated in solid flocks.

COMPOUNDS OF SULPHUR WITH HYDROGEN.

(415) **HYDROSULPHURIC ACID**; *Dihydric Sulphide; Hydrogen Sulphide; Sulphuretted Hydrogen;* $SH_2=34$, $[SH_2]$; *Mol. Vol.* [ ]; *Rel. wt.* 17; *Theoretic density,* 1·1764; *Observed,* 1·1912.—Sulphur forms with hydrogen an important compound commonly termed sulphuretted hydrogen, but which, as it possesses feebly acid properties, is sometimes called hydrosulphuric acid. It is formed in small quantities when sulphur is heated in hydrogen gas, and also together with thiosulphuric acid by the action of steam on sulphur at high temperatures, $3OH_2+4S=2SH_2+H_2S_2O_3$ (Myers, *Compt. Rend.*, 1872, lxxiv. 195), and on passing hydrogen over heated sulphides. It is always prepared for use, however, by decomposing one of the metallic sulphides with an acid, ferrous sulphide and dilute sulphuric acid being usually employed.

Preparation.—1. For ordinary purposes, about half an ounce (15 grams) of ferrous sulphide, FeS, in small fragments, is placed in a bottle together with about 6 or 8 ounces (200 cub. centim.) of water; a fluid ounce (about 30 cub. centim.) of sulphuric acid is now poured in through the funnel tube, when the gas is abundantly evolved: the iron and hydrogen change places, ferrous sulphate is formed and dissolved, and sulphuretted hydrogen is evolved; $FeS+H_2SO_4=SH_2+FeSO_4$. The gas which is prepared in this manner is usually mixed with free hydrogen, produced by the action of the acid on the metallic iron with which the ferrous sulphide is contaminated.*

Fig. 316 shows a convenient arrangement for disengaging a continuous current of the gas from ferrous sulphide. The cork through which the tubes pass is not fitted at once into the bottle, B or C, but is made to fit, as at *a*, into a piece of stout glass tube, open at both ends, such as is shown in fig. 317; this tube is ground so as to close the neck of the bottle air-tight, like an ordinary stopper. The apparatus, which requires to be frequently dismounted in order to be charged afresh, may thus be kept in a serviceable condition without the trouble or loss of time consequent on the frequent renewal of the corks, which would be needed unless this expedient were adopted. The various small tubes are connected together by long pieces of vulcanized caoutchouc tubing.

2.—When the gas is required in a state of purity, 1 part of powdered antimonious sulphide is substituted for the ferrous sulphide: in this case, it is necessary to employ 3 or 4 parts of hydrochloric acid of density 1·1, and to apply a gentle heat to the mixture; the apparatus may then be arranged as in fig. 318.

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* According to Myers (*Ann. Chem. Pharm.*, 1871, clix. 127) the sulphuretted hydrogen evolved from ferrous sulphide and dilute sulphuric acid sometimes contains arsenic, probably as arseniuretted hydrogen formed from arsenic present in the sulphuric acid.

In either case, the gas requires to be washed before collecting it, in order to remove any particles of the acid or of the metallic salt which may have been

Fig. 316.

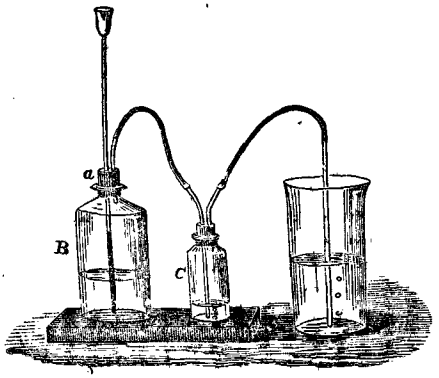
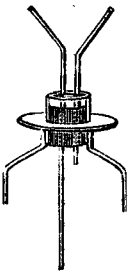


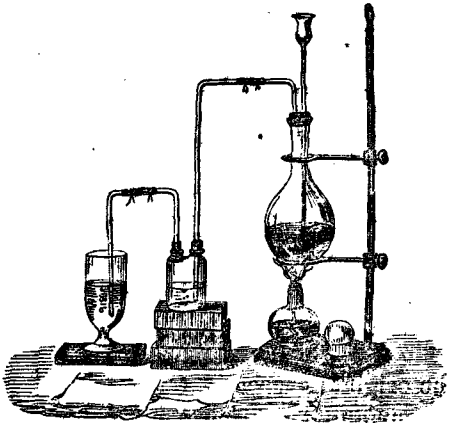
Fig. 317.



mechanically carried over. As the compound of antimony with sulphur is a sesquisulphide, Sb_2S_3, 1 molecule of it requires 6 molecules of hydrochloric acid for its decomposition, and furnishes 2 molecules of antimonious chloride and 3 of sulphuretted hydrogen;

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3SH_2.$$

Fig. 318.



3.—Skey (*Chem. News*, 1873, xxvii. 161) proposes to substitute a mixture of granulated zinc and fragments of native plumbic sulphide (*galena*) for ferrous sulphide, acting on it with dilute hydrochloric acid (1 to 20). An energetic and regular current of sulphuretted hydrogen may thus be obtained.

4.—When large quantities of sulphuretted hydrogen are required, it may be prepared very conveniently by heating paraffin with sulphur in an iron vessel.

Properties.—Hydrosulphuric acid is a transparent, colourless gas, of a very offensive odour, resembling that of rotten eggs. It is highly poisonous when respired in a concentrated form, and even when diluted with from 600 to 1200 times its bulk of air is rapidly fatal to the lower animals. It is inflammable, and burns with a pale bluish flame, depositing sulphur if the supply of air be insufficient for complete combustion. If passed through tubes heated to redness, it is partly decomposed into sulphur and free hydrogen; and when submitted to the action of the silent

electric discharge, it is resolved into hydrogen, sulphur, and hydric persulphide (Berthelot).

Hydrosulphuric acid is also immediately decomposed by chlorine, bromine, and iodine; sulphur being precipitated, and hydrochloric, hydrobromic, or hydriodic acid being formed by the union of the hydrogen with one of the halogens above mentioned.

Its density a little exceeds that of atmospheric air, 1 litre at 0° and 760$^{mm.}$ Bar. weighing 1·5475 grams or 100 cub. in., weighing at 60° F. and 30 inches rather more than 37 grains.

Under a pressure of about 17 atmospheres, sulphuretted hydrogen is reducible to a colourless, extremely mobile liquid, which, according to Regnault, boils at −62° (−79°·6 F.); it freezes to a transparent mass at a temperature of −86° (−122°·8 F.).

Water at 0° (32° F.) dissolves 4·37 times its bulk of sulphuretted hydrogen; 3·23 times its bulk at 15° (59° F.), and 2·66 at 24° (75°·2 F.) (Schönfeld). It is much more soluble in alcohol, which dissolves 17·89 times its volume at 0° (32° F.), 10·97 at 12° (53°·6 F.), and 7·415 at 20° (68° F.). The aqueous solution is feebly acid, and has the smell and taste of the gas. When exposed to the air, this solution becomes turbid from separation of sulphur, whilst the hydrogen of the sulphuretted hydrogen is slowly oxidized, forming water. If the oxidation of sulphuretted hydrogen takes place in a moist atmosphere, a little sulphuric acid is formed, and this action is favoured by the presence of a base which fixes the newly-formed acid.

Composition.—The proportion of hydrogen in a given volume of the gas may be ascertained by heating some granulated tin in a small retort filled with sulphuretted hydrogen and inverted in a vessel of mercury: the sulphur combines with the tin, whilst the hydrogen which remains occupies the same space when cold as the original gas.* In sulphuretted hydrogen 1 volume of sulphur vapour and 2 volumes of hydrogen are therefore condensed into the space of 2 volumes, and the composition of the gas may be thus represented:

		By weight.		By vol.
Sulphur	S	= 32	or 94·12	... 1
Hydrogen	H_2	= 2	5·88	... 2
	SH_2	= 34	100·00	... 2

Sulphuretted hydrogen is formed spontaneously under a variety of circumstances. Whenever a soluble sulphate remains

* Potassium cannot be substituted for tin in this case, because, although it decomposes the gas, the dipotassic sulphide which is formed absorbs and enters into combination with another portion of the gas.

in contact with decaying animal or vegetable matter, the sulphate loses oxygen, which combines with the elements of the decaying substance, whilst sulphide of the metal remains; one atom of calcic sulphate, for example, by the abstraction of 4 atoms of oxygen becomes converted into calcic sulphide; thus $CaSO_4 - 2O_2 = CaS$.

In this way soluble sulphides are formed in many springs, such as those of Harrogate, giving to them their peculiar sulphureous odour: and, in a somewhat similar manner, sulphuretted hydrogen is generated in large quantities in stagnant sewers and cesspools.

The sulphides thus formed are readily decomposed by acids—even the carbonic acid absorbed from the atmosphere being sufficient to occasion the liberation of sulphuretted hydrogen, causing the odour observed on exposing such compounds to moist air.

(416) **Hydrosulphates and Sulphides.**—Hydrosulphuric acid, although possessing but feebly acid properties, reacts readily with bases: for example, if the gas be passed into a solution of ammonia or of potassic hydrate, it is rapidly absorbed, potassic sulphide, K_2S, or ammonic sulphide, $(NH_4)_2S$, being formed, with elimination of water. Moreover, sulphuretted hydrogen in cases in which it occasions a precipitate in the solution of a metallic salt, produces an insoluble metallic sulphide: for instance, when cupric sulphate in solution is treated with sulphuretted hydrogen, an abundant black precipitate of hydrated cupric sulphide is formed, and the liquid becomes acid from the liberation of sulphuric acid: $CuSO_4 + SH_2 + xOH_2 = H_2SO_4 + CuS.xOH_2$. The larger number of the metallic sulphides when thus formed combine with water at the moment of their precipitation.

Sulphuretted hydrogen is in continual requisition in the laboratory as a test for the detection of certain metals, as it gives characteristic precipitates with many metallic salts; for instance, with the compounds of lead it gives a black, with those of arsenicum, a yellow, and with those of antimony an orange-coloured precipitate. Many metallic solutions, such as those of zinc, iron, and manganese, when acidulated, yield no precipitate with sulphuretted hydrogen: and it is therefore commonly employed, in the course of analysis, to separate those metals which are thrown down by it in the form of insoluble sulphides. For this purpose a current of the gas is passed through the solution on which it is designed to act, but as this gas is liable to carry over particles held in mechanical suspension, it is first washed by allowing it to bubble up through a layer of water in a Woulfe's bottle inter-

posed between the generator and the liquid to be submitted to its action, as shown at *c*, fig. 316.

When in any salt the attraction between the metal and the salt-radicle is too great to be overcome by the action of hydrosulphuric acid, the sulphide may be obtained if we simultaneously present an alkali-metal to the salt-radical; this may easily be effected by adding a soluble sulphide to the solution of the salt to be decomposed; if ferrous sulphate, $FeSO_4$, be exposed to a current of sulphuretted hydrogen, it will experience no change, but if mixed with a solution of dipotassic sulphide, a black precipitate of hydrated ferrous sulphide, $FeS.xOH_2$, is immediately produced, whilst potassic sulphate is formed in the solution: $FeSO_4 + K_2S.xOH_2 = K_2SO_4 + FeS.xOH_2$. The sulphides thus formed are very commonly hydrated compounds, and many of them absorb oxygen rapidly when exposed to the air in their moist condition; solutions of the alkaline sulphides have indeed been employed for removing oxygen from gaseous mixtures. The results of oxidation vary, some being converted, like nickel sulphide into sulphate; $NiS.xOH_2 + 2O_2 = NiSO_4 + xOH_2$: whilst others, like ferrous sulphide, are simply converted into free sulphur and a metallic oxide; $4FeS.xOH_2 + 3O_2$ becoming $2Fe_2O_3.xOH_2 + 2S_2$.

Hydrosulphuric acid is usually stated to have a strong disposition to combine with the soluble sulphides, and to form definite compounds with them. These compounds, however, are most conveniently represented by regarding them as double sulphides of the metal and hydrogen, intermediate between hydrosulphuric acid and the ordinary sulphide—*e.g.*:

HHS	;	KHS	;	KKS,
Hydrosulphuric acid.		Potassic sulphhydrate.		Dipotassic sulphide.

corresponding with the compounds in the oxygen series indicated by the formulæ:

HHO	;	KHO	;	KKO.
Water.		Potassic hydrate.		Anhydrous potash.

To this class of double sulphides belongs the ordinary test-liquid, ammonic hydric sulphide, NH_4HS, which is used in the laboratory under the name of hydrosulphate of ammonia. These compounds emit a strong odour of sulphuretted hydrogen, and when decomposed by a metallic salt, the hydrosulphuric acid is set at liberty; for example; $2NH_4HS + MnSO_4 = (NH_4)_2SO_4 + MnS + SH_2$. This evolution of sulphuretted hydrogen distinguishes them from the simple sulphides. No such double sulphides are formed with

hydrogen and the dyads or tetrads, such as the metals of the earths proper and of the iron group.

Tests.—Many of the sulphhydrates and sulphides are easily detected by the odour of sulphuretted hydrogen which they evolve when moistened with hydrochloric acid. A very minute trace of the gas may be detected by enclosing a piece of paper moistened with a solution of plumbic acetate in the upper part of the tube or vessel in which the suspected sulphide has been mixed with acid; if sulphuretted hydrogen be evolved, a brown or black tinge occurs upon the paper after the lapse of a few minutes, owing to the formation of plumbic sulphide. The proportion of free sulphuretted hydrogen, or of a soluble sulphide, in any solution may be accurately determined by mixing the liquid to be tested with a small quantity of a cold solution of starch slightly acidulated with acetic acid, and adding a standard solution of iodine dissolved in potassic iodide until the starch assumes a blue tint from the action of excess of iodine; in this reaction the sulphuretted hydrogen converts the iodine into hydriodic acid, whilst the liquid becomes turbid from the separation of sulphur; $2SH_2 + 2I_2 = 4HI + S_2$.

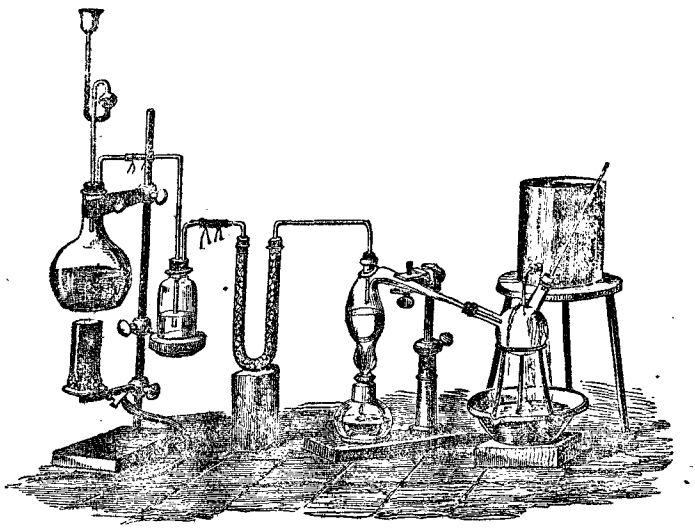
Traces of soluble sulphides may be detected in neutral or alkaline solutions by the magnificent purple colour which they form on the addition of a solution of sodic nitroprusside. When heated before the blowpipe, most of the sulphides emit the odour of sulphurous anhydride.

(417) **HYDRIC PERSULPHIDE,** or *Persulphide of Hydrogen* (H_2S_2? or H_2S_5?) $\left[\begin{matrix}SH\\SH\end{matrix}\right]$; *Density of Liquid,* 1·769.—In order to procure this compound it is usual to begin by preparing a calcic pentasulphide, CaS_5, which may be obtained by boiling equal weights of slacked lime and powdered sulphur in water; calcic pentasulphide mixed with a corresponding amount of calcic thiosulphate (hyposulphite) is formed, and enters into solution; $3CaH_2O_2 + 6S_2 = CaS_2O_3 + 2CaS_5 + 3OH_2$: whilst the excess of undissolved sulphur is separated by filtration. On pouring the deep yellow liquid into hydrochloric acid previously diluted with twice its bulk of water and gently warmed, hydric persulphide subsides as an oily liquid, having a smell and taste resembling that of hydrosulphuric acid: it burns with a blue flame. In many of its properties it presents a striking analogy with hydric peroxide (355); it possesses bleaching powers, is very prone to spontaneous decomposition into sulphur and sulphuretted hydrogen; it is rendered more stable by the presence of acids, and is immediately decomposed by alkalies. The latter circumstance renders it necessary in preparing this compound to add the calcic pentasulphide to the acid, and not the acid to the pentasulphide, which would produce an evolution of hydrosulphuric acid and a precipitation of finely divided sulphur. The sulphur which is precipitated in this manner from an alkaline pentasulphide was formerly employed in medicine under the term of *lac sulphuris* or 'milk of sulphur.'

Oxides of manganese and silver decompose hydric persulphide by mere contact with the liquid, producing a violent effervescence, owing to the disengagement of sulphuretted hydrogen. Hydric persulphide dissolves sulphur freely, so that its composition is not known with certainty, since a portion of sulphur derived from the calcic thiosulphate (hyposulphite) formed in preparing the pentasulphide is always precipitated along with the persulphide, and becomes dissolved in it; and, owing to its instability, the persulphide cannot be purified by distillation.

(418) **SULPHUR CHLORIDE**; *Sulphur Sulphochloride*, $S_2Cl_2 = 135$, $\left[\begin{matrix}SCl\\SCl\end{matrix}\right]$; *Mol. Vol.* [ ]; *Rel. wt.* 67·5; *Density of Liquid*, 1·7055; *of Vapour*, 4·70; *Boiling-pt.* 138° (280°·4 F.).—Chlorine and sulphur form three compounds with each other; they combine gradually at the ordinary temperature, and much

FIG. 319.



more readily when heated. In preparing the chloride, S_2Cl_2, the arrangement shown in fig. 319 may be adopted, in which a steady current of washed and dried chlorine is passed into the retort containing melted sulphur; the resulting chloride must be collected in a dry receiver, kept cool externally: it may be purified from excess of chlorine by redistillation from powdered sulphur; a yellow volatile liquid, of a peculiar, disagreeable, penetrating odour is thus formed. It emits fumes on exposure to the air, owing to its action on the atmospheric moisture. When dropped into water, it falls to the bottom, and is slowly decomposed into hydrochloric and sulphurous acids, mixed with some of the polythionic acids, and free sulphur in the electropositive form. It

acts powerfully on mercury when brought into contact with it, and dissolves sulphur freely; with ammonia it combines in two proportions, forming the compounds $2NH_3.S_2Cl_2$, and $4NH_3.S_2Cl_2$. An oxychloride of sulphur, $S_2O_3Cl_4$ (441), is obtained in crystals by passing moist chlorine through the chloride.

(419) **SULPHUR DICHLORIDE** ($SCl_2 = 103$; *Density of Liquid*, 1·625) may be formed by saturating the preceding compound with chlorine at a low temperature, such as that produced by a mixture of ice and salt, and then removing the excess of chlorine by passing a current of carbonic anhydride through the liquid at 0° (32° F.) (Huebner and Gueront, *Zeits. Chem.*, 1870, vi. 455; Dalzell and Thorpe, *Phil. Mag.*, 1871, 309). It is a deep-red liquid, which fumes strongly in the air, and is decomposed in the direct rays of the sun into the chloride S_2Cl_2 and free chlorine. When heated to 64° (147·°2 F.) it boils, but is at the same time partially decomposed.

(420) **SULPHUR TETRACHLORIDE,** SCl_4.—On saturating the chloride, S_2Cl_2, with chlorine at −22° (−7·°6 F.), a light brown, transparent liquid is obtained, which on analysis yields numbers agreeing with the formula SCl_4; that this is not merely a solution of chlorine in the dichloride, SCl_2, is shown by the action of sulphuric anhydride on it, which is represented by the equation:

SCl_4	+	S_2O_6	=	$SOCl_2$	+	$S_2O_5Cl_2$
Sulphur tetrachloride.		Sulphuric anhydride.		Thionylic chloride.		Pyrosulphurylic chloride.

The preparation of the dichloride from the tetrachloride by passing a current of carbonic anhydride through it is explained by the fact that the tetrachloride begins to dissociate at temperatures above −22° (−7·°6 F.) into the dichloride and chlorine, the latter of which is carried off by the carbonic anhydride as fast as it is liberated (Michaelis and Schifferdecker, *Deut. chem. Ges. Ber.*, v. 924, and vi. 993; Michaelis, *Ann. Chem. Pharm.*, 1873, clxx. 1).

(421) **COMPOUNDS OF SULPHUR WITH OXYGEN.**—Three oxides only of sulphur are known in the anhydrous state, viz.:

			Mol. wt.	Mol. vol.	Sulphur.		Oxygen.	
Sulphuric sesquioxide	...	S_2O_3	= 112		57·14	+	42·86	= 100
Sulphurous anhydride	...	SO_2	= 64		50·00	+	50·00	= 100
Sulphuric anhydride	...	SO_3	= 80		40·00	+	60·00	= 100

Sulphur, however, forms numerous oxidized acid compounds: two of them (sulphurous acid and sulphuric acid) have been long known and employed on a large scale in the arts; the others are less important, and of comparatively recent discovery. Some of these acids of sulphur are interesting, inasmuch as they exhibit a combining ratio different from any which we have as yet considered, and they show the application of the law of multiple proportions to the case of the sulphur, as well as to that of the oxygen which they contain.

The following table exhibits the composition of the various oxyacids of sulphur, the existence of which is at present known. The five compounds which stand last on the list are often spoken

of as constituting the *polythionic* series (from πολύ, many, θεῖον, sulphur), in allusion to the multiple proportion in which the sulphur enters their composition:

Hyposulphurous acid, Hydrosulphurous acid ...	$H_2SO_2 = 66$
Sulphurous acid	$H_2SO_3 = 82$
Sulphuric acid	$H_2SO_4 = 98$
Thiosulphuric acid, or Sulphosulphuric acid (Hyposulphurous acid)	$H_2S_2O_3 = 114$
Dithionic „	$H_2S_2O_6 = 162$
Trithionic „	$H_2S_3O_6 = 194$
Tetrathionic „	$H_2S_4O_6 = 226$
Pentathionic „	$H_2S_5O_6 = 258$

We shall first examine sulphurous acid, then sulphuric acid, briefly noticing the other acids, whose compounds, with the exception of some of the thiosulphates (hyposulphites), have as yet received no practical applications.

(422) **SULPHUROUS ANHYDRIDE** (formerly *Sulphurous Acid*): $SO_2=64$; *Mol. Vol.* [ ]; *Rel. wt.* 32; *Theoretic Density of Gas,* 2·2144; *Observed,* 2·247; *of Liquid,* 1·4336 at 0° (32° F.); *Melting-pt.* −76° (−105° F.); *Boiling-pt.* −8° (17°·6 F.).—Sulphur burns in oxygen with a lilac-coloured flame, producing a gaseous oxide; when the combustion is terminated, and the gas has been allowed to regain its original temperature, the volume of the gaseous product will be found to be the same as before the experiment, but the density of the gas is doubled. This experiment furnishes an easy proof of the composition of the gas; for it is thus shown to contain equal weights of sulphur and oxygen. Sulphurous anhydride is the sole product if the oxygen be dry.

The composition of sulphurous anhydride may be represented in the following way:

		By weight.	By vol.
Sulphur	$S = 32$ or 50	...	1
Oxygen	$O_2 = 32$ 50	...	2
Sulphurous anhydride	SO_2 64 100	...	2

Preparation.—1. When required in a pure state, sulphurous anhydride is always prepared by depriving sulphuric acid of part of its oxygen. In order to effect this, two or three ounces (about 90 grams) of concentrated sulphuric acid may be boiled in a glass retort with half an ounce (15 grams) of copper clippings or of mercury. The final result of the reaction in the case of copper is indicated by the following equation:

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2OH_2.*$$

* According to Maumené, a certain quantity of cuprous sulphide, Cu_2S, is produced during this operation, after which a mixture of cupric sulphide and

Sulphur may be substituted for the metal in this process introducing at the same time some fragments of pumice, but the delivery tube should be wide, as otherwise it is apt to become choked with the sublimed sulphur. The reaction is:

$$2H_2SO_4 + S = 3SO_2 + 2OH_2.$$

If a cast-iron vessel be employed, this forms one of the best methods for the preparation of pure sulphurous anhydride on a large scale. The gas should be washed in the usual way by allowing it to bubble up through a bottle containing a small quantity of water, to retain sulphuric acid and any impurities which might be mechanically suspended in the gas.

2.—Sulphuric acid may be more economically deoxidized by means of charcoal or dry sawdust, but the gas in this case is accompanied by one-half its volume of carbonic anhydride; $C + 2H_2SO_4 = 2SO_2 + CO_2 + 2OH_2$. For most purposes, however, such as the preparation of the alkaline sulphites, the presence of carbonic anhydride is unimportant.

3.—Sulphurous anhydride may also be procured readily by the oxidation of sulphur: for example, by heating in a flask an intimate mixture of 4 parts of flowers of sulphur and 5 of finely powdered peroxide of manganese, sulphurous anhydride and manganous sulphide are produced; $S_2 + MnO_2 = SO_2 + MnS$. A somewhat similar result is obtained by heating a mixture of 3 parts of cupric oxide with 1 part of sulphur; $2CuO + S_2$ becoming $Cu_2S + SO_2$.

Sulphurous anhydride is emitted abundantly from the craters of volcanoes, and is occasionally met with in solution in the springs of volcanic districts.

4.—On the large scale, as in the manufacture of oil of vitriol, sulphurous anhydride is prepared by burning iron pyrites in a current of air in properly constructed furnaces.

By passing sulphurous anhydride through a tube surrounded by a mixture of ice and salt, it may be condensed to a colourless, transparent, limpid liquid, which dissolves bitumen; it freezes at $-76°$ ($-105°$ F.), forming a transparent, colourless, crystalline solid, heavier than the liquid; in closed tubes, at $15°{\cdot}5$ (60° F.), it exerts a pressure of 2·54 atmospheres. The density of liquid sulphurous anhydride, according to Andréeff (*Ann. Chem. Pharm.*, 1859, cx. 1), is 1·4336 at 0° (32° F.), 1·4055 at 10° (50° F.), and 1·3914 at 15° (59° F.). Pierre gives 1·4911 at $-20°{\cdot}5$ ($-4°{\cdot}9$ F.). Fig. 320 shows a

oxysulphide is also formed. According to Millon and Commaille, every trace of arsenic in the sulphuric acid, or in the copper dissolved, accumulates in this insoluble residue.

method of liquefying sulphurous anhydride. The gas is generated in the flask, A, washed and dried by means of concentrated sulphuric acid placed in the bottle, B, passed through the pewter worm, C, which is surrounded by a freezing mixture of ice and salt, and collected in the receiver, D, which is also cooled by a

FIG. 320.

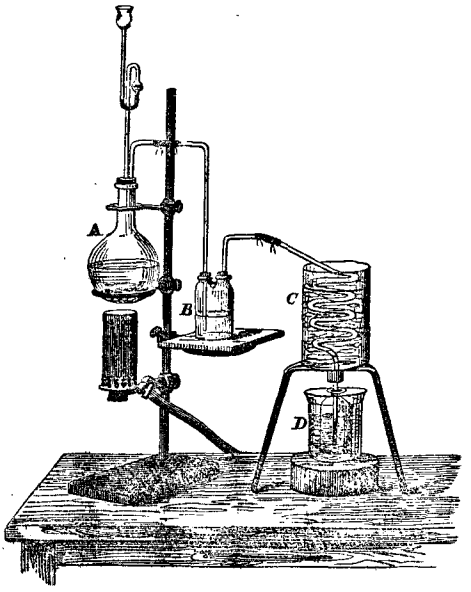


FIG. 321.

freezing mixture; the liquefied compound is stored up for use in small tubes, one of which is shown at E, fig. 321: the tube having been placed in the freezing mixture, the anhydride is poured into it through a small tube funnel, and the liquid is preserved by drawing off and sealing the tube at the narrow portion in the flame of the blowpipe, without removing it from the freezing mixture.

Properties.—This gas has the pungent, suffocating odour given off by burning sulphur, which renders it quite irrespirable in a concentrated form; when diluted, it produces the symptoms of ordinary catarrh. It is not inflammable, and quickly extinguishes the flame of burning bodies. When submitted to the action of the silent electrical discharge, a small portion (about one-tenth) is resolved into its elements, sulphur and oxygen. Sulphurous anhydride dissolves in water yielding a solution of *sulphurous acid*, H_2SO_3, which readily decomposes again at a very gentle heat into the anhydride and water. The solution has a taste and smell similar to that of the gas, and gradually absorbs oxygen from the air, by which the sulphurous is converted into sulphuric acid. On cooling a saturated aqueous solution of the gas to 0° (32° F.), Döpping succeeded in procuring the pure acid,

H_2SO_3, in the form of cubical crystals; a crystalline hydrate of sulphurous acid ($SO_2.15OH_2$, Schönfeld; or $SO_2.8OH_2$, Pierre) may also be obtained at a low temperature: at 4° (39° F.) this hydrate melts and is decomposed. Water, according to Schönfeld, takes up, at 0° (32° F.), 79·79 times its bulk of the gas; 56·65 times its bulk at 10° (50° F.); 47·28 at 15° (59° F.); and 39·37 at 20° (68° F.). Sulphurous anhydride dissolves also in concentrated sulphuric acid: the latter absorbing 58 times its volume of the gas. Owing to the solubility of sulphurous anhydride in water, the gas must always be collected either over mercury, or in dry bottles by displacement; from the high density of the gas (double that of oxygen), the latter method is easily applied.

Sulphurous anhydride and sulphuretted hydrogen, in the presence of moisture, decompose each other, half the oxygen of the sulphurous anhydride uniting with the hydrogen of the sulphuretted hydrogen, water and pentathionic acid being formed, whilst sulphur is deposited. For complete decomposition, equal volumes of sulphuretted hydrogen and of sulphurous anhydride would be requisite; $10SO_2 + 10H_2S = 5S_2 + 8OH_2 + 2H_2S_5O_6$. Much of the sulphur thus deposited is in the electropositive form (414), and is insoluble in carbonic bisulphide. It is probable that a large proportion of native sulphur has been formed in consequence of this reaction. Tyndal has shown that sulphurous anhydride is decomposed by light; a white cloud consisting of sulphur and sulphuric anhydride being formed, when a beam of sunlight is allowed to pass through a tube filled with the gas.

Uses.—Sulphurous acid possesses considerable bleaching powers, and is extensively employed in bleaching straw and wool, as well as silken goods, isinglass, sponge, and other articles which would be injured by chlorine. The articles to be bleached are moistened, and suspended in closed chambers in which sulphur is burned in an open dish; the sulphurous anhydride is absorbed by the damp goods, and their colour is discharged. The acid appears to act by forming colourless compounds with certain colouring matters. It does not, like chlorine, decompose the colouring matter, for the sulphurous acid may either be expelled by a stronger acid, or it may be neutralized by an alkali, and the colour will be restored; the reproduction of the yellow colour in new flannel, when it is washed with an alkaline soap for the first time, affords a practical illustration of the effect of an alkali upon goods which have been bleached by sulphurous acid. Sulphurous anhydride is a powerful antiseptic; and is also highly

valuable as a disinfecting agent. Meat which has been exposed to the action of the gas, and then sealed up in metallic canisters filled with nitrogen to which a little nitric oxide has been added to remove the last traces of oxygen, may be preserved fresh for years. It is often employed to check fermentation in cider, or in home-made wine; a little sulphur being burned in the cask before filling it with the liquor; hydric calcic sulphite is now largely used by brewers for a similar purpose.

It is, however, principally as a preliminary step in the manufacture of oil of vitriol that sulphurous anhydride is made upon the large scale, and in this case it is always obtained by burning sulphur, or a metallic sulphide, in air.

(423) **Sulphites.**—Sulphurous acid is a weak dibasic acid. With the alkalies, it forms two kinds of salts, one of which is represented by the ordinary disodic sulphite, $Na_2SO_3.10OH_2$, $[SO(ONa)_2,10OH_2]$, whilst the other class is represented by the hydric potassic sulphite, $KHSO_3$, $[SO(OH)(OK)]$ often called the bisulphite. The sulphites of the alkali-metals are the only ones which are freely soluble in water; but those of barium, strontium, and calcium, are dissolved to some extent by an aqueous solution of sulphurous acid.

The following table shows the composition of some of the sulphites.

	General formulæ.	
Sulphurous acid	H_2SO_3	$[SO(OH)_2]$
Normal salt	M_2SO_3	$[SO(OM)_2]$
Acid salt	$HMSO_3$	$[SO(OH)(OM)]$
Double salt	$MM'SO_3$	$[SO(OM)(OM')]$
Potassic sulphite	$K_2SO_3.2OH_2$	$[SO(OK)_2.2OH_2]$
Hydric-potassic sulphite (bisulphite)	$KHSO_3$	$[SO(OH)(OK)]$
Sodic sulphite	$Na_2SO_3.10OH_2$	$[SO(ONa)_2.10OH_2]$
Hydric-sodic sulphite (bisulphite)...	$NaHSO_3.4OH_2$	$[SO(OH)(ONa).4OH_2]$
Calcic sulphite	$CaSO_3.2OH_2$	$[SO(O_2Ca)''.2OH_2]$
Baric sulphite	$BaSO_3$	$[SO(O_2Ba)'']$
Magnesic sulphite	$MgSO_3.3OH_2$	$[SO(O_2Mg)''.3OH_2]$
Plumbic sulphite	$PbSO_3$	$[SO(O_2Pb)'']$
Argentic sulphite	Ag_2SO_3	$[SO(OAg)_2]$

Many of the sulphites are decomposed by a strong heat, the acid being gradually expelled. They are also decomposed by sulphuric or hydrochloric acid, with evolution of sulphurous acid, which is known by its peculiar pungent odour. Hydric potassic sulphite when kept in solution in a closed vessel slowly undergoes decomposition, sulphuric and trithionic acids being formed and sulphur deposited. The best test for detecting small traces of

sulphites consists in the addition of a fragment of zinc and a drop or two of hydrochloric acid to the solution; the sulphurous acid is deoxidized, the sulphur combines with hydrogen, and sulphuretted hydrogen is given off; the gas last named may be detected by suspending a piece of paper moistened with a solution of plumbic acetate, in the upper part of the vessel, which should be closed by a glass plate. Salts of silver in solution give a white precipitate with solutions of the soluble sulphites; the precipitate is soluble in excess of the sulphite, and it is partially reduced to metallic silver when the liquid is boiled; a characteristic reaction is the formation, with baric chloride of a white precipitate of baric sulphite, which is soluble in hydrochloric acid, but the solution thus obtained gives a white precipitate of baric sulphate on the addition of a solution of chlorine, of iodine, or of bleaching powder. The sulphites, when moist, absorb oxygen from the air; and solutions of these salts are often used as deoxidizing agents; for example, the ferric salts are reduced by them to ferrous salts; arsenic acid is reduced to arsenious acid, and chromic acid to a green salt of chromium. Gold, selenium, and tellurium, are precipitated in the reduced state from solutions containing excess of hydrochloric acid.

A solution of sulphurous acid dissolves and is decomposed by the metals which, like zinc, iron, tin, and cadmium, evolve hydrogen with hydrochloric acid. Iron, for example, is rapidly dissolved if heated with a solution of sulphurous acid, ferrous sulphite and thiosulphate (hyposulphite) being first formed, the latter, however, is speedily resolved into ferrous sulphide and tetrathionate; the tetrathionate in its turn is converted into ferrous sulphate, free sulphur, and sulphurous acid, as represented in the annexed equations:

$$\underset{\text{Iron.}}{2Fe} + \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{3H_2SO_3} = \underset{\substack{\text{Ferrous}\\\text{hyposulphite.}}}{FeS_2O_3} + \underset{\substack{\text{Ferrous}\\\text{sulphite.}}}{FeSO_3} + \underset{\text{Water.}}{3OH_2},$$

and

$$\underset{\substack{\text{Ferrous}\\\text{hyposulphite.}}}{3FeS_2O_3} = \underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{FeS} + \underset{\substack{\text{Ferrous}\\\text{tetrathionate.}}}{FeS_4O_6} + \underset{\substack{\text{Ferrous}\\\text{sulphite.}}}{FeSO_3}$$

whilst further, $FeS_4O_6 + OH_2 = FeSO_4 + H_2SO_3 + S_2$.

The sulphites are readily formed by passing a stream of sulphurous acid through water in which the oxide or the carbonate of the metal is dissolved or suspended, the carbonates being decomposed with effervescence.

(424) **SULPHURIC ACID**; *Dihydric Sulphate;* $H_2SO_4=98$ $[SO_2(OH)_2]$.—This substance, which constitutes one of the most important products of chemical manufacture, is made in enormous

quantities. In Great Britain alone upwards of 100,000 tons are annually consumed. The acid is occasionally met with uncombined in thermal springs, particularly in those of volcanic regions. The sulphates of calcium, barium, magnesium, and some other metals, are amongst the most abundant constituents of the crust of the earth.

Preparation.—When sulphur is boiled in *aqua regia*, or in concentrated nitric acid, it is gradually oxidized and converted into sulphuric acid; but this method is never employed, excepting for experimental purposes in the laboratory. On the large scale, it is made by a process first employed by Roebuck, about the year 1746, since which period the mode of conducting it has undergone several modifications and improvements, although in principle it continues the same.

The changes which occur in this process are remarkable and instructive. It has been already mentioned, that when sulphur is burned in air or in oxygen, the product is sulphurous anhydride. This gas, if made to combine with half as much more oxygen as it already contains, is converted into sulphuric anhydride. Direct union between the two gases, however, does not easily take place, so that the intervention of some third substance becomes necessary; if water be presented to them, a very gradual combination occurs. If pure and dry oxygen, mixed with twice its bulk of sulphurous anhydride, be passed over spongy platinum heated in a tube, the two gases combine, and sulphuric anhydride, SO_3, is produced. Advantage has been taken of this reaction for the preparation of sulphuric anhydride on the large scale (428). Wöhler has also observed, that the two gases unite rapidly when passed through a tube heated to incipient redness, and containing a mixture of oxide of copper and sesquioxide of chromium, obtained by precipitation.

The following table represents the composition of sulphuric acid:

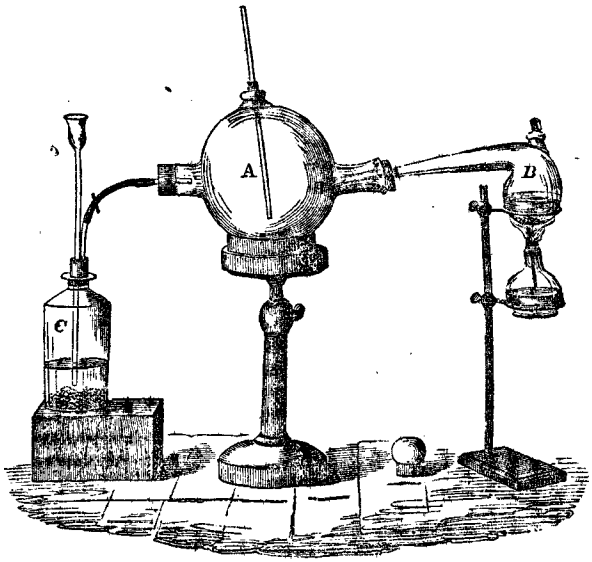
	Anhydride.		Oil of vitriol.	
Sulphur ...	$S = 32$	or 40	$S = 32$	or 32·65
Oxygen ...	$O_3 = 48$	60	$O_4 = 64$	65·31
			$H_2 = 2$	2·04
Sulphuric anhydride	$SO_3 = 80$	100	$H_2SO_4 = 98$	100·00

If sulphurous anhydride mixed with oxygen in a moist state come in contact with nitric oxide, or any other of the higher oxides of nitrogen, combination will take place with great rapidity; and further, a small proportion of the oxide of nitrogen

will suffice to effect the combination of an almost indefinite amount of sulphurous anhydride and oxygen, if water be also present. Upon these facts the process employed in the manufacture of sulphuric acid is founded.

The reaction is easily watched upon the small scale by means of the following apparatus. Into a large three-necked receiver, A, fig. 322, filled with atmospheric air, and slightly moistened in the interior, sulphurous anhydride from the retort, B, and nitric oxide from the bottle, C, are made to pass; ruddy fumes of nitric peroxide, NO_2, are immediately formed by the combination of

FIG. 322.



the nitric oxide with atmospheric oxygen, and in a few minutes the inner surface of the receiver becomes coated with a white crystalline deposit into the composition of which sulphurous anhydride, nitric peroxide, and water enter. As soon as this crystalline mass is treated with water, it is decomposed with brisk effervescence; $NO_2 + SO_2 + xOH_2$, yielding $NO + H_2SO_4 + (x\text{-}1)OH_2$; 1 molecule of nitric oxide escapes, and 1 molecule of sulphuric acid remains in solution: the nitric oxide, by again absorbing oxygen from the air, is reconverted into nitric peroxide; this combines with another molecule of sulphurous anhydride in the presence of a small quantity of water; fresh crystals are formed, and these in their turn are decomposed by the water as before. The nitric oxide is thus again liberated, and may go through the same round of compositions and decompositions, until the whole of the oxygen in the air has been consumed: the oxide of nitrogen thus acts the part of a carrier of oxygen to the sulphurous anhydride. In the manufacture of sulphuric acid on the large scale, no deposition of crystals actually occurs, as the formation of the crystalline body and its destruction are simultaneous if the operation be properly conducted.*

* The true composition of this crystalline body has been the object of much discussion and numerous experimental inquiries. H. Rose states that by passing

(425) **Manufacture of Sulphuric Acid.**—In the manufacture of sulphuric acid, the sulphurous anhydride is procured by burning either sulphur or iron pyrites, FeS_2; provision being made for supply of atmospheric air, sufficient not only to burn the sulphur, but also to oxidize the sulphurous anhydride thus produced to sulphuric anhydride. The general arrangements adopted are shown in fig. 323. A, A, represent furnaces in which the sulphur or pyrites is burned: in the current of heated gas an iron pot, *b*, is placed, which has been previously charged with a mixture of sodic nitrate and oil of vitriol. Vapours of nitric acid are thus liberated, which pass on with the sulphurous anhydride, by suitable flues, into immense chambers, F, F, constructed of sheet lead, and supported by a strong timber

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pure dry nitric oxide into a glass vessel, from which oxygen is carefully excluded, and the interior of which is moistened with sulphuric anhydride, SO_3, a white, hard, amorphous substance is formed; and this compound he regards as the essential constituent in the crystals above described. It fuses at a high temperature, and may be sublimed without decomposition. Brüning has shown that during the formation of this compound sulphurous anhydride is liberated, in the proportion of 1 molecule for every 2 molecules of nitric oxide absorbed; and he found the crystalline compound to have a composition which may be represented by the formula, $N_2O_3.2SO_3 = (NO)_2S_2O_7$. Water immediately decomposes it, liberating nitric oxide, whilst sulphuric acid is dissolved. If the anhydrous crystals be exposed to the air, they absorb moisture and emit nitrous fumes. Concentrated sulphuric acid, by the aid of heat, dissolves them in all proportions without change; the solution crystallizes, on cooling, in rectangular prisms, which appear to contain water of crystallization.

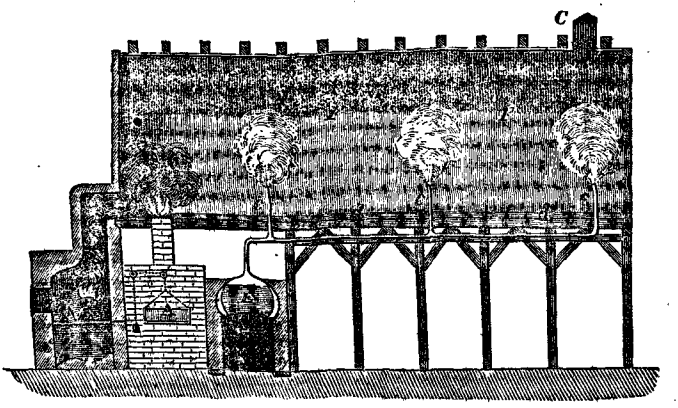
Oil of vitriol rapidly absorbs both nitrous anhydride and nitric peroxide, and forms a crystalline compound similar to the foregoing; the addition of water immediately liberates red fumes of nitric peroxide from it.

There are many other methods by which this curious substance may be obtained, but they often involve very complicated considerations. De la Provostaye procures it by the action of liquid sulphurous anhydride on liquid nitric peroxide: he considers it when anhydrous to consist of, $SO_3.SO_2.2NO_2$, which is consistent with the analysis of Brüning.

Weltzien found that sulphuric acid, H_2SO_4, combines directly with nitrous anhydride, N_2O_3, forming a white crystalline mass, in proportions which may be represented by the formula $OH_2.2SO_3.N_2O_3$, or $H(NO)SO_4$. According to the same chemist, sulphuric acid also forms with nitric peroxide a white crystalline compound fusible at 73° (163°·4 F.), which, even when the peroxide is present in large excess, contains the two substances in a proportion which may be represented by the formula, $2OH_2.3SO_3.2NO_2$.—(*Ann. Chem. Pharm.*, 1860, cxv. 216.) Tilden (*Jour. Chem. Soc.*, 1864, xxvii. 630) has obtained *nitrosyl sulphate*, $H(NO)SO_4$, by passing the gases evolved on heating 'aqua regia' into sulphuric acid: the crystals melt at 85°—87° (185°—188°·6 F.), but decompose immediately after with evolution of a yellow vapour. Stenhouse and Groves (*ibid.* 1877, i. 545) prepare the crystals by passing into sulphuric acid, the gas produced by acting at 70° (158° F.) on arsenious anhydride with nitric acid of density 1·30.

framework. These chambers are often 12 or 15 feet high, 15 or 20 wide, and from 150 to 300 feet in length, or about 4 or

FIG. 323.



5 metres high, 5 or 7 broad, and from 50 to 100 metres long; they are sometimes partially intersected by incomplete transverse leaden partitions, interposed in the current of the mixed gases, with a view of effecting their more intimate admixture. Water to the depth of 2 or 3 inches (6 or 8 cm.) is placed upon the floor of the chamber, *d, d,* to condense the acid; and the mutual reaction of the atmospheric oxygen, sulphurous anhydride, and nitric oxide is further facilitated by the injection of steam at a pressure of about 10 lb. upon the square inch by means of jets, *c, c, c,* supplied from the boiler, E. The nitric acid from the nitre speedily becomes deoxidized by the sulphurous anhydride to the state of nitric oxide ($3SO_2 + 2HNO_3 + 2OH_2 = 2NO + 3H_2SO_4$), and then the changes already pointed out succeed each other rapidly, and sulphuric acid is formed in large quantity.

In a properly managed chamber, the gases which pass off by the exit flue, C, consist only of nitrogen and nitric oxide, the sulphurous anhydride and oxygen being supplied in quantities just sufficient for their mutual combination, fresh atmospheric air entering at the other end along with the sulphurous anhydride. When pyrites is employed, the sulphurous anhydride produced always contains a small quantity of sulphuric anhydride.

Gay-Lussac has taken advantage of the solubility of nitric oxide in oil of vitriol, to economize the consumption of nitre in the process, which upon the old plan amounted to from one-eighth to one-twelfth of the weight of the sulphur consumed.

This improvement consists in conducting the spent gases into a leaden tower filled with fragments of coke, through which a stream of concentrated sulphuric acid is continually trickling. The acid thus becomes charged with the nitrous vapours, and flows off at the bottom of the tower to a reservoir from which it is pumped into an apparatus, where it is decomposed by steam, and the evolved nitrous fumes passed again through the chamber; or the decomposition is effected by allowing it to flow together with water over a 'cascade' of earthenware in the leaden chamber. When the sulphuric acid is not required in a state of purity, as in the manufacture of soda or superphosphates, it may be very conveniently denitrated by allowing it to flow, together with acid from the chamber, of density 1·5 about, into a 'Glover's tower,' a leaden tower some 15 or 20 feet high, lined with stone and filled with flints or pumice; the hot gases from the pyrites ovens pass through this tower, where they not only remove the nitrous acid, converting it into nitric oxide, but at the same time concentrate the dilute acid; sulphurous anhydride, steam, and nitric oxide passing into the chamber. The flow of acid is so arranged that it issues from the bottom of the tower of a density of 1·7. The gases, to avoid cooling, pass directly from the ovens into the towers, so that the acid concentrated by this means contains iron and other impurities, which are ordinarily deposited in the flue. The quantity of nitre formerly requisite has thus been reduced by one-half, or even by two-thirds. There is, however, always a loss of nitric acid, and this, from Fremy's experiments (*Compt. Rend.*, 1870, lxx. 61), would appear to be due to the reduction of nitrous acid to nitrous oxide, N_2O_2, by the sulphurous acid in presence of excess of water.

The sulphuric acid which collects at the bottom of the chambers is in too dilute a condition for many technical purposes, as it is not found advantageous to allow it to attain a degree of concentration greater than 1·55, when it becomes liable to absorb and retain the nitrous fumes.* At this point it is sufficiently strong for the manufacture of salt-cake, but it requires concentration for other purposes; with this view, if a 'Glover's tower' is not employed, it is drawn off and evaporated in shallow leaden pans until it has acquired a density of 1·720; the concentration cannot be carried beyond this point in these vessels, because the temperature required would endanger the melting of the leaden

* Crude acid of density 1·60 does not usually contain more than 0·6 per cent. of nitrous acid (Allhusen).

pan and its corrosion by the acid. This acid of density 1·720 forms the *brown* acid of commerce; it is extensively employed in the manufacture of the so-called superphosphate of lime for manures, and for other coarse purposes. When required in a still more concentrated form, the brown acid is transferred to glass retorts, or, as is practised in many works, into platinum stills; the presence of nitrous compounds must be avoided when platinum is employed, otherwise the metal is gradually corroded; in these, it is again further heated until white fumes of oil of vitriol begin to pass over. It is useless to carry the operation beyond this point, as the concentrated acid then begins to distil over. Indeed, during the whole operation some acid passes over with the water, which is therefore preserved, and returned to the leaden chamber.

The acid that remains in the retort after it has thus been boiled down, is the concentrated *oil of vitriol* of commerce. De Marignac (*Ann. Chim. Phys.*, 1853, [3], xxxix. 189) finds that it

Strength of Sulphuric Acid of Different Densities (Kolb, *Ding. poly. Jour.*, 1873, ccix. 368).

Density.	SO_3 in 100 parts.	H_2SO_4.	Density.	SO_3 in 100 parts.	H_2SO_4.	Density.	SO_3 in 100 parts.	H_2SO_4.
1·007	1·5	1·9	1·190	21·1	25·8	1·453	45·2	55·4
1·014	2·3	2·8	1·200	22·1	27·1	1·468	46·4	56·9
1·022	3·1	3·8	1·210	23·2	28·4	1·483	47·6	58·3
1·029	3·9	4·8	1·220	24·2	29·6	1·498	48·7	59·6
1·037	4·7	5·8	1·231	25·3	31·0	1·514	49·8	61·0
1·045	5·6	6·8	1·241	26·3	32·2	1·530	51·0	62·5
1·052	6·4	7·8	1·252	27·3	33·4	1·540	52·2	64·0
1·060	7·2	8·8	1·263	28·3	34·7	1·563	53·5	65·5
1·067	8·0	9·8	1·274	29·4	36·0	1·580	54·9	67·0
1·075	8·8	10·8	1·285	30·5	37·4	1·597	56·0	68·6
1·083	9·7	11·9	1·297	31·7	38·8	1·615	57·1	70·0
1·091	10·6	13·0	1·308	32·8	40·2	1·634	58·4	71·6
1·100	11·5	14·1	1·320	33·9	41·6	1·652	59·7	73·2
1·108	12·4	15·2	1·332	35·1	43·0	1·671	61·0	74·7
1·116	13·2	16·2	1·345	36·2	44·4	1·691	62·4	76·4
1·125	14·1	17·3	1·357	37·2	45·5	1·711	63·8	78·1
1·134	15·1	18·5	1·370	38·3	46·9	1·732	65·2	79·9
1·142	16·0	19·6	1·383	39·5	48·3	1·753	66·7	81·7
1·152	17·0	20·8	1·397	40·7	49·8	1·774	68·7	84·1
1·162	18·0	22·2	1·410	41·8	51·2	1·796	70·6	86·5
1·171	19·0	23·3	1·424	42·9	52·8	1·819	73·2	89·7
1·180	20·0	24·5	1·439	44·1	54·0	1·842	81·6	100·0

always contains a slight excess of water beyond that required by the formula H_2SO_4: instead of 18·36 per cent. of water, he always obtained 19·62; and a similar observation was made by Gay-Lussac. Playfair states that, if the concentration of the

acid be effected by a temperature not exceeding 260° (500° F.), the true compound H_2SO_4 of density 1·848 is obtained; but if heated to ebullition, it is partially decomposed in the manner stated by De Marignac.

The table on the preceding page gives the proportion of sulphuric acid and of sulphuric anhydride contained in solutions of the densities therein mentioned in 100 parts by weight; the original memoir (also *Jour. Chem. Soc.*, 1874, xxvii. 193) likewise gives the amount of acid in one kilogram of the sulphuric acid of different densities, the densities corresponding to degrees Baumé, &c.

(426) **Properties of Sulphuric Acid.**—This acid, the oil of vitriol of commerce, forms a dense, oily-looking, colourless liquid, without smell, and of specific gravity 1·842. It is intensely caustic, and chars almost all organic substances from its powerful attraction for moisture. It mixes with water in all proportions, and the mixture, when cold, has a less volume than the two liquids when separate. Great heat is given out at the moment the mixture is made; the dilution should therefore be performed gradually, always pouring the acid into the water, and not the water into the acid. So powerful is the attraction of the acid for moisture, that if it be freely exposed to the air for a few days in a shallow dish, it frequently doubles its weight by the absorption of aqueous vapour. In the laboratory, advantage is very often taken of this property, which enables it to be employed in a variety of cases as a desiccating agent (66 and 185). The acid of commerce is sometimes of a dark brown colour, occasioned by its charring action on fragments of organic matter, such as straw or wood, which have accidentally fallen into it. Sulphuric acid does not evaporate at the ordinary temperature, so that if a drop of the dilute acid fall upon a cloth, the water gradually evaporates until the acid which is left behind acquires a certain degree of concentration; on approaching a fire or other source of heat, a further portion of the water is expelled, and the acid becomes more and more concentrated, until it chars or destroys the fibres; this is one cause of the destructive action of sulphuric acid upon linen, even when very much diluted.

De Marignac finds that the true sulphuric acid, H_2SO_4, when heated emits a small quantity of the vapour of the anhydride, and the remaining liquid boils at 338° (640°·4 F.). Bineau states that just above the boiling-point of the acid the vapour has a density of 2·15, which would represent 2 volumes of the anhydride and 2 volumes of steam (1 molecule of each) condensed into the space

of 3 volumes, but it continues to expand by heat until at 470° (878° F.) a molecule of the compound occupies the space of 4 volumes, which would reduce the density of the vapour to 1·692. This by some chemists is supposed to be produced by the separation of the compound into aqueous vapour and anhydride by the process of dissociation (see *note*, Part I. p. 112). After the acid has been frozen, it melts at 10°·5 (51° F.), but it may be cooled much below this point without solidifying. On dropping into the cooled acid a crystal of the acid previously frozen, congelation immediately occurs, and the temperature rises to 10°·5 (51° F.). The concentrated acid of commerce does not usually freeze until it has been cooled to about −34° (−29°·2 F.); but when frozen it does not become liquid until the temperature reaches 0° (32° F.).

(427) **Nordhausen Sulphuric Acid.**—For the purpose of dissolving indigo in the process of dyeing Saxony blue, an acid of still higher concentration than oil of vitriol is required. Such an acid was largely prepared at the town of Nordhausen, in Saxony, and is hence known as *Nordhausen oil of vitriol*, or fuming sulphuric acid. It is now made chiefly in Bohemia. The old name for ferrous sulphate was *green vitriol*, and this circumstance, taken in conjunction with the oily consistence of the concentrated acid, gave rise to the name of *oil of vitriol*, by which the concentrated acid of commerce is still frequently known, and which is convenient as distinguishing it from more dilute acids. In preparing the Nordhausen acid, ferrous sulphate is dried at a moderate heat to expel its water of crystallization, and is then distilled in earthen retorts; a dense, brown, fuming liquid passes over, of a density of about 1·9.

(428) **SULPHURIC ANHYDRIDE**, $SO_3=80$; *Rel. wt.* 40; *Theoretic Density of Vapour*, 2·768; *Observed*, 3·01: *Mol. Vol.* [ ].—If the fuming Nordhausen acid be placed in a glass retort, furnished with a receiver which is kept cool by ice, and a gentle heat be applied to the retort, white fumes pass over, which solidify into a white, silky-looking, fibrous mass. This is the compound formerly called *anhydrous sulphuric acid*. The residue in the retort, after all the anhydride is expelled, consists of ordinary oil of vitriol. Sulphuric anhydride may also be obtained from the hydric sodic sulphate, $NaHSO_4$, which melts at a dull red heat, and is deprived of its hydrogen in the form of water; after which, if distilled in an earthen retort, it yields white fumes of the anhydride, whilst disodic sulphate remains in the retort:

$$2NaHSO_4=Na_2SO_4.SO_3+OH_2, \text{ and}$$
$$Na_2S_2O_7=Na_2SO_4+SO_3.$$

It is likewise formed on passing a mixture of dry oxygen and sulphurous anhydride over spongy platinum or platinized asbestos.

Messrs. Messel and Squire, taking advantage of this reaction, have succeeded in preparing sulphuric anhydride from oil of vitriol in the following manner:—The vapour of ordinary sulphuric acid is passed through a white-hot platinum tube, whereby it is almost completely decomposed into water, oxygen, and sulphurous anhydride; the mixed gases, after passing through a leaden worm to condense the greater part of the water, are completely dehydrated in a leaden tower filled with coke over which a stream of concentrated sulphuric acid is allowed to trickle. The dry mixture of oxygen and sulphurous anhydride is now passed through platinum tubes heated to low redness and containing fragments of platinized pumice, when the gases combine to form sulphuric anhydride which is condensed in a series of Woulffe's bottles. Winkler (*Ding. poly. Jour.*, 1875, ccxvii. 128) had previously proposed a very similar process.

Sulphuric anhydride possesses no acid properties. As obtained by the distillation of the Nordhausen acid, it is tough, ductile, and can be moulded in the fingers, like wax, without charring the skin. Pure sulphuric anhydride obtained by repeated distillation of the ordinary anhydride in hermetically sealed tubes, according to Weber (*Pog. Ann.*, 1876, clix. 313), is a mobile colourless liquid at the ordinary temperature, but solidifies on cooling to a mass of long transparent crystals resembling those of nitric anhydride, and totally different in appearance from the asbestos-like needles of the ordinary anhydride. Its density at 16° (60°·8 F.) is 1·940. It fumes in the air, and is very deliquescent: when thrown into water, the heat emitted is so intense that it hisses as a hot iron would do. The solution has all the properties of ordinary sulphuric acid. The anhydride melts at 14°·8 (58°·6 F.), and boils at 46°·2 (115°·2 F.) under a pressure of 761·6 mm., forming a colourless vapour, which if passed through ignited porcelain tubes, is decomposed into 2 volumes of sulphurous anhydride and 1 of oxygen; 1 volume of sulphur vapour and 3 of oxygen being condensed in the anhydride into the space of 2 volumes of vapour. The specific gravity of this vapour was found by Mitscherlich to be 3·01, or somewhat higher than its calculated amount, which is 2·764: for

		By weight.		By volume.
Sulphur	$S = 32$	or 40	...	1
Oxygen	$O_3 = 48$	60	...	3
Sulphuric anhydride ...	$SO_3 = 80$	100	...	2

De Marignac, and subsequently Schultz Sellack (*Pog. Ann.*, 1870, cxxxiv. 480) stated that sulphuric anhydride existed under two modifications, one of which formed long colourless prisms which melt at about 16° (60°·8 F.), and boil at 46° (114°·8 F.); the other crystallized in exceedingly slender white

needles which at 50° (122° F.) gradually became liquid, and were transformed into the first modification. These differences, however, Weber considers to be due to traces of moisture in the supposed second modification, the first being evidently the pure anhydride.

Sulphuric anhydride in some cases combines with the anhydrous bases; if its vapour be passed over baryta heated nearly to redness, the two combine with incandescence, and baric sulphate is formed. Mercury when heated in the vapour, is converted into mercuric sulphate with liberation of sulphurous anhydride. Phosphorus takes fire in its vapour, setting sulphur free.

Sulphuric anhydride dissolves iodine, and unites with one-tenth of its weight of the latter to form a green crystalline compound. It also combines with hydrochloric acid, and forms a liquid termed *chlorhydrosulphuric* acid, $HCl.SO_3$, $[SO_2(OH)Cl]$ (442), first obtained by Williamson by the action of phosphoric chloride upon sulphuric acid; $H_2SO_4 + PCl_5 = HCl.SO_3 + HCl + POCl_3$; hydrochloric acid and phosphoric oxytrichloride being formed at the same time.

Sulphuric anhydride unites with oil of vitriol to form *pyrosulphuric acid*, or *anhydro-sulphuric acid*, a compound having the formula $H_2SO_4.SO_3$ or $H_2S_2O_7$ $\left[\begin{matrix}SO_2(OH)\\O\\SO_2(OH)\end{matrix}\right]$. It crystallizes in plates which fuse at 35° (95° F.). Salts of potassium, silver, and barium corresponding to this acid are known. The composition of the Nordhausen acid approximates to the formula just given. A compound of the formula $H_2S_4O_{13}$ or $H_2SO_4.3SO_3$ has also been obtained (Weber).

(429) **SULPHURIC SESQUIOXIDE**, $S_2O_3 = 112$.—Ordinary sulphuric anhydride combines with sulphur forming a solution of a blue or green colour. This colour is due to a particular compound of sulphur and oxygen, *sulphuric sesquioxide*, S_2O_3, which Weber (*Pog. Ann.*, 1875, clvi. 531) has isolated by taking advantage of its insolubility in pure sulphuric anhydride. It is prepared by adding flowers of sulphur in small quantities at a time to the pure anhydride maintained at a temperature of 15° (59° F.); after a short time the colourless anhydride is poured off, and the excess adhering to the sesquioxide expelled at a gentle heat. A bluish green crystalline mass is thus obtained which slowly decomposes at the ordinary temperature, giving off sulphurous anhydride and leaving sulphur. The sesquioxide dissolves in a mixture of sulphuric acid and anhydride, forming a blue, green, or brown solution according to the amount of sulphuric anhydride present.

(429*a*) **Hydrates of Sulphuric Acid.**—If water be added to sulphuric acid, until the density is reduced to 1·78, a definite hydrate, $H_2SO_4.OH_2$, is formed, which crystallizes in splendid rhombic prisms: from this property it is often termed *glacial sulphuric acid*. The crystals melt at 7°·5 (45°·4 F.), and have a density of 1·951. This hydrate begins to boil at about 205° (400° F.) giving off a weaker acid. Graham found that it might be obtained by heating a more dilute acid at 204°·5 (400° F.) until it ceases to give off water.

Another *hydrate*, $H_2SO_4.2OH_2$, may, according to Graham, be obtained by evaporating a dilute acid *in vacuo* at 100° (212° F.) until it ceases to lose weight. The density of this hydrate is 1·62, and it begins to boil at 193° (379°·4 F.).

These two hydrates may be regarded as separate acids bearing the same kind of relation to sulphuric acid as pyro- and orthophosphoric acids do to metaphosphoric acid. Their formulæ would then be H_4SO_5, $[SO(OH)_4]$, and

H_6SO_6, $[S(OH)_6]$: their corresponding zinc salts are known, $Zn_2SO_6 = ZnSO_4.ZnO$, $[SO(O_2Zn)''_2]$, and $Zn_3SO_6 = ZnSO_4.2ZnO$, $[S(O_2Zn)''_3]$.

We are therefore acquainted with the following definite compounds of sulphuric anhydride with water; starting with the anhydride:

Compound.	Formula.	Fusing point.		Boiling point.		Specific gravity.
		°C.	°F.	°C.	°F.	
Sulphuric anhydride ...	SO_3	14·8	58·6	46·2	115·2	1·940
Anhydro-sulphuric acid	$H_2SO_4.SO_3$	35	95			
Oil of vitriol	H_2SO_4	10·5	51	338	640·4	1·848
Glacial acid	$H_2SO_4.OH_2$	8·3	47	205	401	1·780
Graham's hydrate ...	$H_2SO_4.2OH$			193	379·4	1·620

Uses.—The applications of sulphuric acid in the arts are very numerous. Immense quantities of it are consumed in the manufacture of sodic sulphate as a preliminary process in making sodic carbonate; and it is in constant requisition for the preparation of nitric, hydrochloric, and other volatile acids. Its applications in the laboratory are too numerous to be specified.

(430) **Impurities in Commercial Sulphuric Acid.**—The oil of vitriol of commerce is never pure: it always contains lead, derived from the vessels in which it is made, and ammonia. The greater part of the plumbic sulphate is precipitated as a white powder when the acid is diluted. It is also frequently contaminated with arsenious acid, derived from the pyrites; the diluted acid in this case gives a yellow precipitate when exposed to a current of sulphuretted hydrogen. The arsenic is still more easily recognised by what is termed Marsh's test, which will be described under the head of arsenic. On the large scale, this impurity is effectually removed by adding to the acid a small quantity of baric sulphide, or better still, baric thiosulphate; orpiment, As_2S_3, and baric sulphate are formed, and as they are both insoluble in the acid, they may be separated by subsidence and decantation. The greater part of the arsenious acid may also be got rid of by adding hydrochloric acid and boiling the liquid, when the arsenic is expelled in the form of arsenious chloride along with the excess of hydrochloric acid. Traces of selenium are sometimes found in French sulphuric acid. Nitric acid and some of the lower oxides of nitrogen are also often present: a strong solution of ferrous sulphate in water, when poured on to the undiluted acid in a tube, so as to avoid mixing, shows the presence of these impurities by striking a characteristic purplish-red colour at the point of contact of the two liquids.

Sulphurous acid may sometimes be detected in the acid, as may also hydrochloric acid and potassic sulphate.

When required pure, the acid must be re-distilled with a little ammonic sulphate; this salt decomposes any nitrous acid which may be present (p. 154). The distillation requires to be conducted with much care, as the boiling takes places with violent concussions and sudden bursts of vapour; the danger may be avoided by distilling it from freshly broken crystals of quartz, or still better by introducing a considerable quantity of platinum cut in thin strips, and heating with a rose-burner. According to McLeod, acid which has been used for desiccating, and has deposited much of its plumbic sulphate, may be concentrated without difficulty by boiling it down in an open flask on an ordinary wire gauze.

(431) **Sulphates.**—Sulphuric acid in its concentrated form acts but feebly upon metallic bodies in the cold, but in some cases it undergoes decomposition when boiled with them: even silver is dissolved by it, sulphurous anhydride being formed, whilst the sulphate of the metal is dissolved in the excess of sulphuric acid thus: $Ag_2 + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2OH_2$. Copper, mercury, arsenicum, antimony, bismuth, tin, lead, and tellurium are acted upon by the acid in a similar manner. Gold, platinum, rhodium, and iridium are not acted upon by sulphuric acid even when boiled with it. The more oxidizable metals are dissolved by this acid when diluted with water, hydrogen being liberated, whilst the metal takes the place of the hydrogen, forming a sulphate: zinc, iron, cobalt, nickel, and manganese are acted upon in this way. The concentrated acid is also decomposed when boiled with charcoal or with sulphur (p. 203), sulphurous anhydride being evolved.

Sulphuric acid is one of the most energetic of the acids, in almost every instance displacing from their salts those acids which boil at a lower temperature than itself. The salts formed by this acid are termed *sulphates*. With the alkali-metals it forms acid salts, such as acid sulphate of potassium, or hydric potassic sulphate, $KHSO_4$: in a few instances basic salts, such as the basic sulphate of copper, $CuSO_4.2CuH_2O_2$, may be obtained. Many of the sulphates occur native, and constitute important and well-known minerals, such as gypsum, $CaSO_4.2OH_2$, and the sulphates of barium, strontium, and lead. Some are formed by the spontaneous or artificial oxidation of the sulphides, as, for instance, the sulphides of iron and copper, which, by exposure to the weather, or by roasting, furnish the sulphates of the metals.

The soluble sulphates of the metals may be readily prepared by dissolving the metal in dilute sulphuric acid, or the oxide or carbonate, in cases in which the metal is not readily attacked by the acid. The insoluble sulphates, such as those of barium and lead, may be obtained by precipitating a soluble salt of the metal by means of some soluble sulphate, such as sodic sulphate. Many of the sulphates are formed as residues during the preparation of the volatile acids by the action of sulphuric acid on their salts. Potassic sulphate is thus obtained during the preparation of nitric acid from saltpetre, sodic sulphate as a residue from common salt in the manufacture of hydrochloric acid, and so on. The sulphates of potassium, barium, strontium, lead, silver, and both mercurous and mercuric sulphate, are anhydrous. Calcic sulphate (gypsum) contains $CaSO_4.2OH_2$. The sulphates of zinc, magnesium, iron, cobalt, and nickel, usually crystallize with $7OH_2$; but the number of molecules of water in these salts is often smaller if the solution be allowed to crystallize at a high temperature, the proportion of water being sometimes 5, at others 4, and under some circumstances as low as $2OH_2$. The sulphates of the group isomorphous with magnesic sulphate contain 1 molecule of water, which admits of displacement by a molecule of some anhydrous sulphate, such as potassic sulphate or ammonic sulphate: peculiar double salts are thus formed, which retain 6 molecules of water of crystallization, and which are still isomorphous with magnesic sulphate (582). Cupric sulphate crystallizes with $5OH_2$, but it forms double salts containing $6OH_2$: such as, $CuSO_4.K_2SO_4.6OH_2$, isomorphous with those just mentioned. Sodic sulphate crystallizes usually as, $Na_2SO_4.10OH_2$, but it exhibits some singular anomalies (622).

Neither plumbic sulphate nor the sulphates of the metals of the alkalies and alkaline earths are decomposed when heated to redness, except magnesic sulphate, which loses part of its acid; the sulphates of zinc, cadmium, nickel, cobalt, copper, and silver require an intense heat to decompose them: but the other sulphates part with their acid without difficulty when strongly ignited. When heated with charcoal, the sulphates are all decomposed; those of the metals of the alkalies and alkaline earths being converted into sulphides, which, when moistened with hydrochloric acid, evolve sulphuretted hydrogen. Baric sulphate may thus be easily recognised, even in small quantity, if, after having been mixed with a little charcoal and folded in a piece of platinum foil, it is heated in the flame of the blowpipe; $BaSO_4+4C=BaS+4CO$; the carbonic oxide escaping as gas;

the baric sulphide, when moistened with hydrochloric acid, is converted into baric chloride, and evolves sulphuretted hydrogen; $BaS+2HCl=BaCl_2+SH_2$. The sulphates of the metals of the alkalies and alkaline earths may also be converted into sulphides by heating them to redness in a glass or porcelain tube, and passing over them a current of dry hydrogen gas. In this way potassic sulphate is reduced without difficulty to sulphide, water being eliminated; $K_2SO_4+4H_2=K_2S+4OH_2$.

Sulphuric acid is dibasic. The composition of some of the more important sulphates is shown in the following list.

		General formulæ.	
Neutral salt		M_2SO_4	$[SO_2(OM)_2]$
Acid salt		$MHSO_4$	$[SO_2(OH)(OM)]$
Double salt		$M'MSO_4$	$[SO_2(OM)(OM')]$
Potassic sulphate ...		K_2SO_4	$[SO_2(OK)_2]$
Sodic		$Na_2SO_4.10OH_2$	
Hydric potassic sulphate (bisulphate)		$KHSO_4$	$[SO_2(OH)(OK)]$
Ammonic sulphate ...		$(NH_4)_2SO_4$	$[SO_2(ONH_4)_2]$
Calcic „ ...		$CaSO_4.2OH_2$	
Baric „ ...		$BaSO_4$	$[SO_2(O_2Ba)'']$
Strontic „ ...		$SrSO_4$	
Plumbic „ ...		$PbSO_4$	
Argentic „ ...		Ag_2SO_4	
Magnesic „ ...		$MgSO_4.7OH_2$	
Zincic „ ...		$ZnSO_4.7OH_2$	
Ferrous „ ...		$FeSO_4.7OH_2$	
Cobalt „ ...		$CoSO_4.7OH_2$	
Cupric „ ...		$CuSO_4.5OH_2$	
Aluminic „ ...		$Al_2(SO_4)_3.18OH_2$	$[S_3O_6(O_6Al_2)^{vi}.18OH_2]$
Potash-alum		$K_2Al_2(SO_4)_4.24OH_2$	$\left[\begin{matrix}SO_2(OK)\\SO_2\\SO_2\\SO_2(OK)\end{matrix}\right](O_6Al_2)^{vi}.24OH_2\Big]$
Cupric dipotassic sulphate		$CuSO_4.K_2SO_4.6OH_2$	$\left[\begin{matrix}SO_2(OK)\\SO_2(OK)\end{matrix}\right](O_2Cu''.6OH_2\Big]$
Basic sulphate of copper		$CuSO_4.2CuH_2O_2$	$[S(OH)_2[OCu(OH)]_2(O_2Cu)'']$

Tests.—Sulphuric acid and its salts are easily recognised when in solution by the white precipitate of baric sulphate which is formed on the addition of baric nitrate; this precipitate is insoluble in nitric acid. A white precipitate of plumbic sulphate, nearly as insoluble as baric sulphate, is formed on adding a soluble salt of lead to a solution containing sulphuric acid or a sulphate. The sulphates of strontium, calcium, and silver are but sparingly soluble in water; the others are readily soluble; nearly all the sulphates are insoluble in alcohol, unless a large excess of acid be present. The sulphates which are insoluble in

water and in acids may be entirely decomposed by fusion with an excess of sodic or potassic carbonate, a sulphate of the alkali-metal being formed, which may be dissolved by water, whilst an insoluble carbonate of the other metal is left. A solution of either potassic or sodic carbonate, when boiled with the insoluble sulphates, produces a similar but less complete decomposition.

(432) **HYPOSULPHUROUS ACID** or *Hydrosulphurous acid*, H_2SO_2.—This acid, discovered by Schützenberger, is the true hyposulphurous acid, the acid $H_2S_2O_3$, usually known by that name, being thiosulphuric acid. On dissolving zinc in aqueous sulphurous acid no hydrogen is evolved, and a yellow solution is obtained, possessed of great reducing power due to the presence of zincic hyposulphite.

Tolerably pure sodic hyposulphite, $NaHSO_2$, may be obtained by dissolving metallic zinc in a concentrated solution of sodic hydric sulphite, separating it from the zincic sodic sulphate which crystallizes out, and adding about three times its volume of alcohol. This precipitates the remainder of the sulphate, and on pouring off the solution and allowing it to stand in a cool place for some hours, it solidifies to a mass of slender needles of the sodic hyposulphite. It may be purified by solution in water that has been previously boiled to expel air, and reprecipitation by alcohol. In all these operations the vessels employed should be quite filled with the liquid, and the air should be carefully excluded. The sodic salt is very soluble in water, but insoluble in alcohol, and when exposed to the air in a moist state, absorbs oxygen with great rapidity, causing considerable elevation of temperature. Sodic hyposulphite is also formed at the negative pole on submitting a solution of sodic sulphite to electrolysis.

On treating the sodic salt with oxalic acid, a solution of hyposulphurous acid is obtained, of a deep orange-yellow colour: it is much more unstable than the sodic salt, rapidly losing its colour and depositing sulphur.

The acid is probably analogous in constitution to formic acid, $H.COOH$ $\left[\begin{Bmatrix} H \\ CO(OH) \end{Bmatrix}\right]$ containing tetrad sulphur in the place of the carbon, $H.SOOH$, $\left[\begin{Bmatrix} H. \\ SO(OH) \end{Bmatrix}\right]$.

(433) **THIOSULPHURIC** or **SULPHOSULPHURIC ACID**, hitherto called **HYPOSULPHUROUS ACID**;

$$H_2S_2O_3 = 114,\ [SSO(OH)_2].$$

Of the remaining acids of sulphur, the only one of any practical

importance is the thiosulphuric, sulphosulphuric, hyposulphurous, or *dithionous* acid. Its sodium salt has been largely employed in the fixing of photographic pictures. This application has arisen from the power possessed by this compound of dissolving those argentic haloid salts which are insoluble in water, forming with them soluble double salts; the surface of the photograph is freed from the unaltered argentic compound by immersion in a solution of the 'hyposulphite,' whilst the portion which has been blackened by light is left unacted upon; if, after this operation, the picture be well washed with water, it is no longer liable to alteration by exposure to light.

Besides its application in photography, the sodic thiosulphate ('hyposulphite') is employed to a considerable extent as *antichlore*, for removing the last traces of chlorine from the bleached pulp employed in paper-making; and it has been proposed by Percy as a solvent in the separation of argentic chloride for metallurgical purposes.

Rose states that none of the thiosulphates can be obtained in the anhydrous form, all of them retaining at least 1 molecule of water which cannot be expelled without completely decomposing the salt, so that their true formula should be $M'_2S_2H_2O_4$; that of the barium salt, for instance, instead of being $Ba''S_2O_3.OH_2$, should be $Ba''S_2H_2O_4$. This, however, has been shown by Pape to be an error, the lead salt dried at 100° (212° F.) containing $Pb''S_2O_3$. The salts may therefore be regarded as sulphates in which 1 atom of oxygen is replaced by 1 atom of dyad sulphur, and may be called thiosulphates or sulphosulphates.

Plumbic sulphate	$PbSOO_3$	$[SO_2(O_2Pb)''$
Plumbic thiosulphate or sulphosulphate	$PbSSO_3$	$[SS''O(O_2Pb)'']$
Sodic sulphate	Na_2SOO_3	$[SO_2(ONa)_2]$
Sodic thiosulphate or sulphosulphate ...	Na_2SSO_3	$[SS''O(ONa)_2]$

Sodic Thiosulphate or *Hyposulphite* (*hyposulphite of soda*; $Na_2S_2O_3.5OH_2$; *Density*, 1·672), is largely manufactured from soda waste, and to some extent from impure sodic sulphide (prepared by fusing together in a covered crucible equal weights of sodic carbonate and powdered sulphur, or by converting sodic sulphate into sulphide, by calcining the sulphate with carbon), by passing a stream of gaseous sulphurous anhydride through its aqueous solution, until the gas ceases to be absorbed; the liquid is then filtered and evaporated, when sodic thiosulphate crystallizes out in striated rhombic prisms terminated by oblique faces. A still better plan consists in digesting a solution of sodic sulphite with

powdered sulphur; the sulphur is gradually dissolved and forms a colourless solution, which on evaporation yields crystals of sodic thiosulphate, 1 atom of sulphur combining with 1 molecule of sodic sulphite; Na_2SO_3+S becoming $Na_2S_2O_3$. According to Letts (*Jour. Chem. Soc.*, 1870, xxiii. 424), sodic thiosulphate loses all its water when heated at 100° (212° F.). At higher temperatures it is resolved into sodic sulphate and pentasulphide; $4Na_2S_2O_3=3Na_2SO_4+Na_2S_5$. According to Edison, it is soluble to a considerable extent in oil of turpentine.

The **Thiosulphates of Calcium** and **Strontium** ($CaS_2O_3.6OH_2$ and $SrS_2O_3.5OH_2$), may be prepared by passing sulphurous anhydride through the sulphides of calcium and strontium suspended in water; their solutions are decomposed below 100° (212° F.), into free sulphur and sulphites of the earths.

Calcic thiosulpate is formed spontaneously in large quantity in the refuse lime from the gas-works, and in the refuse from the ball soda of the alkali works when exposed to the air; these residues consist chiefly of a mixture of calcic sulphide with lime and calcic carbonate, and are now employed as valuable sources of sodic thiosulphate, which is readily obtained from them by double decomposition with sodic carbonate or sulphate. Instead of exposing the calcic sulphides to the air they may be converted directly into thiosulphate by treatment with sulphurous acid.

Baric Thiosulphate, ($BaS_2O_3.OH_2$) [$SSO(O_2Ba)''OH_2$], may be obtained in small brilliant crystals by mixing dilute solutions of baric chloride and sodic thiosulphate. It is impossible, however, to obtain the acid in the form of a hydrate either from this or from any of its salts; when, for example, sulphuric acid is added to baric thiosulphate, baric sulphate is precipitated; but if the solution be filtered, the clear liquid speedily becomes milky from the separation of sulphur, and the odour of sulphurous anhydride is emitted; $H_2S_2O_3$ becoming decomposed into $S+SO_2+OH_2$.

The soluble thiosulphates are easily recognized by the facility with which they dissolve argentic chloride, forming the argentic sodic thiosulphite, which may be obtained in crystals, and yields a solution of an intensely sweet taste;

$$AgCl+Na_2S_2O_3=NaCl+NaAgS_2O_3.$$

Solutions of the thiosulphates give a white precipitate of plumbic thiosulphate in solutions of the salts of lead; this precipitate may be dried at 100° (212° F.) without change, but at a higher temperature it becomes decomposed and blackened, owing to its partial conversion into plumbic sulphide; a solution of mercurous

nitrate is immediately decomposed by a solution of the thiosulphates at ordinary temperatures in a similar manner, the black sulphide of mercury being deposited. When these salts are heated with a solution of a cupric salt acidulated with hydrochloric acid, they give a brown precipitate, consisting of cupric sulphide. An alcoholic solution of iodine is rendered colourless by admixture with an excess of thiosulphate, a tetrathionate of the metal being produced (436).

Aurous Trisodic Thiosulphate, or *Hyposulphite of gold and sodium,* $AuNa_3 2S_2O_3.2OH_2$, was formerly employed for gilding the daguerreotype plate, and is now used for colouring the positive proof obtained in photographic printing. It may be prepared in a state of purity by mixing concentrated solutions of 1 part of auric chloride and 3 parts of sodic thiosulphate: sodic chloride, sodic tetrathionate, and hyposulphite of sodium and gold being formed: on the addition of alcohol the latter salt is precipitated; the precipitate must be redissolved in a small quantity of water, and again precipitated by alcohol. It crystallizes in groups of colourless needles, which are very soluble in water, but insoluble in alcohol. It may be mixed with dilute sulphuric or hydrochloric acid without the evolution of sulphurous acid. The formation of this double salt is explained by the following equation (Fordos and Gélis, *Ann. Chim. Phys.*, 1845, [3], xiii. 399):

$$\underset{\text{Sodic thiosulphate.}}{4Na_2S_2O_3} + \underset{\text{Auric chloride.}}{AuCl_3} = \underset{\text{Aurous trisodic thiosulphate.}}{AuNa_3 2S_2O_3} + \underset{\text{Sodic tetrathionate.}}{Na_2S_4O_6} + \underset{\text{Sodic chloride.}}{3NaCl.}$$

(434) **HYPOSULPHURIC ACID:** *Dithionic acid; Dihydric dithionate;* $H_2S_2O_6 = 162, \left[\begin{cases} SO_2(OH) \\ SO_2(OH) \end{cases}\right]$.—This acid is more stable than thiosulphuric acid, and may be obtained in solution in water. When sulphurous anhydride is passed through water in which finely divided peroxide of manganese is suspended, the gas is rapidly absorbed, and if the liquid be kept cool, manganous hyposulphate is formed; $MnO_2 + 2SO_2$, yielding MnS_2O_6. If the temperature be allowed to rise, manganous sulphate is formed instead; $MnO_2 + SO_2$, becoming $MnSO_4$. It is difficult to prevent the formation of a little of the latter, but the two salts are easily separated; on adding baryta-water manganese is precipitated as hydrated protoxide, and baric sulphate and hyposulphate are formed; $MnSO_4 + MnS_2O_6 + 2BaH_2O_2 = BaSO_4 + BaS_2O_6 + 2MnH_2O_2$; $\left[SO_2(O_2Mn)'' + \begin{cases} SO_2 \\ SO_2 \end{cases}(O_2Mn)'' + 2Ba(OH)_2 = SO_2(O_2Ba)'' + \begin{cases} SO_2 \\ SO_2 \end{cases}(O_2Ba)'' + 2Mn(OH)_2\right]$. The manganous hydrate and baric sulphate being insoluble are readily removed by filtration, and the solution on evaporation below 5° (41° F.) leaves the baric hyposulphate in prismatic efflorescent crystals, $BaS_2O_6.4OH_2$; at higher temperatures it yields permanent crystals, with only two molecules of water, which belong to the oblique system. By the cautious addition of dilute sulphuric acid to a solution

of this salt until a precipitate ceases to be formed, hyposulphuric acid is liberated and may be filtered from the baric sulphate: this when concentrated by evaporation in vacuo leaves an inodorous strongly acid liquid of density 1·347, which is readily resolved into sulphuric acid and sulphuric anhydride,

$$H_2S_2O_6 = H_2SO_4 + SO_2.$$

Many double hyposulphates may be obtained, such as the baric disodic hyposulphate, $BaNa_2S_2O_6.4OH_2$, and the corresponding silver salt, $AgNaS_2O_6.2OH_2$. $\left[\begin{cases} SO_2(Ag) \\ SO_2(ONa) \end{cases} 2OH_2\right]$.

The hyposulphates are all soluble in water. The solid salts when heated emit sulphurous anhydride, whilst a sulphate of the metal remains behind. When in solution, they may be oxidized at a boiling heat by chlorine or by nitric acid, two molecules of sulphuric acid being formed;

$$2H_2S_2O_6 + 2OH_2 + O_2 = 4H_2SO_4.$$

In the cold, they present no appearance of decomposition when treated with sulphuric acid, but if heated with it, sulphurous anhydride is evolved, but no deposit of sulphur occurs. These reactions distinguish the hyposulphates from both the sulphites and thiosulphates.

(435) **TRITHIONIC ACID**; *Dihydric trithionate*; $H_2S_3O_6 = 194$ $\left[\begin{cases} SO_2(OH) \\ S \\ SO_2(OH) \end{cases}\right]$.—If a saturated solution of hydric potassic sulphite, $KHSO_3$, be digested with powdered sulphur for three or four days until the yellow colour which the liquid at first acquires has disappeared, sulphurous anhydride gradually escapes and potassic trithionate, $K_2S_3O_6$, is formed. The action of sulphurous anhydride on potassic thiosulphate yields the same salt: it crystallizes in anhydrous four-sided prisms, terminated by dihedral summits. Trithionic acid is also formed in several other reactions, as when manganous sulphide is digested with a solution of ammonic sulphate:

$$MnS + 2(NH_4)_2SO_4 = (NH_4)_2S_3O_6 + MnO + 2NH_3 + OH_2.$$

Hydrogen sulphide is evolved at the same time, probably owing to a decomposition of the trithionate. When iodine is added to a mixture of sodic sulphite and thiosulphate, sodic trithionate is formed:

$$Na_2SO_3 + Na_2S_2O_3 + I_2 = Na_2S_3O_6 + 2NaI.$$

Again, on adding sulphur dichloride, SCl_2, to a concentrated solution of potassic sulphite in the proper proportion, the mixture becomes warm, and on cooling deposits potassic trithionate in crystals: $2K_2SO_3 + SCl_2 = K_2S_3O_6 + 2KCl$ (Spring, *Deut. chem. Ges. Ber.*, 1873. vi. 1108, and 1874, vii. 1157). Solutions of the trithionates give black precipitates with mercurous nitrate, and white with mercuric nitrate; with argentic nitrate they give a yellowish-white precipitate, which soon becomes black. Potassic trithionate may be decomposed by means of tartaric or hydrofluosilicic acid, and the liberated trithionic acid has even been obtained in prismatic crystals, but its solution gradually undergoes spontaneous decomposition into sulphur, sulphurous acid, and sulphuric acid; $OH_2 + H_2S_3O_6 = S + H_2SO_3 + H_2SO_4$, $\left[OH_2 + \begin{cases} SO_2(OH) \\ S \\ SO_2(OH) \end{cases} = S + SO(OH)_2 + SO_2(OH)_2\right]$. When the trithionates are heated in a closed tube, sulphur is sublimed, sulphurous anhydride is expelled, and sulphate of the metal is left.

(436) **TETRATHIONIC ACID**; *Dihydric tetrathionate*, $H_2S_4O_6 = 226$ $\left[\begin{matrix}SO_2(OH)\\S\\S\\SO_2(OH)\end{matrix}\right]$.—When baric thiosulphate is suspended in water and iodine is added, baric iodide is formed, and a new, sparingly soluble salt, baric tetrathionate, is separated in hydrated crystals which contain 2 molecules of water: $2BaS_2O_3 + I_2 + 2OH_2 = BaS_4O_6\,2OH_2 + BaI_2$. A tetrathionate is also produced when a solution containing a thiosulphate and an iodate is treated with an acid, thus:

$$12Na_2S_2O_3 + K_2I_2O_6 + 12HCl = 6Na_2S_4O_6 + 2KI + 12NaCl + 6OH_2.$$

The baric tetrathionate may be purified by recrystallization; and from a solution of this salt, a pure solution of tetrathionic acid may be prepared by the addition of a quantity of sulphuric acid just sufficient to precipitate the whole of the barium; the acid may be concentrated *in vacuo* over sulphuric acid. On boiling the solution, sulphur is deposited, sulphurous anhydride escapes, and sulphuric acid remains in the liquid.

(437) **PENTATHIONIC ACID**: $H_2S_5O_6 = 258$, $\left[\begin{matrix}SO_2(OH)\\S\\S\\S\\SO_2(OH)\end{matrix}\right]$.—A solution of sulphurous acid is decomposed by passing through it a current of sulphuretted hydrogen; sulphur is deposited, and a new acid remains in the liquid; $10H_2SO_3 + 10SH_2 = 2H_2S_5O_6 + 5S_2 + 18OH_2$: on digesting the milky liquid with metallic copper and subsequently precipitating by sulphuretted hydrogen any of the metal which may have been dissolved, a clear solution is obtained, which may be concentrated in a vacuum until it attains a density of 1·6. This acid is very unstable, its solution being readily decomposed into tetrathionic and trithionic acids, whilst sulphur is deposited. *Baric pentathionate*, $BaS_5O_6.2OH_2$, may be obtained in silky scales by neutralizing the acid with baryta-water, and precipitating the salt from its aqueous solution by the addition of alcohol: mecurous nitrate gives a yellow precipitate in its solution, and argentic nitrate a yellow precipitate, which quickly becomes decomposed and turns black.

Tests for the Acids of Sulphur.—The action of sulphuric acid upon the salts of the various oxy-acids of sulphur, affords a simple means of distinguishing between most of these acids. When concentrated sulphuric acid is poured upon the sulphates, they evolve no odour, even when heated with it. The sulphites, with dilute sulphuric acid, yield an odour of sulphurous anhydride even in the cold. The hyposulphates emit no odour of sulphurous anhydride with dilute sulphuric acid in the cold, but evolve sulphurous anhydride by the aid of heat: whilst dilute sulphuric acid produces with the thiosulphates, even in the cold, an odour of sulphurous anhydride attended with a deposit of sulphur.

(438) **SULPHUROUS DICHLORIDE**, or *Thionylic chloride*, $SOCl_2$, is a colourless, strongly refracting liquid, boiling at 78° (172°·4 F.), its

density at 0° (32° F.) is 1·675. This chloride is readily prepared by the action of sulphurous anhydride on phosphoric pentachloride, and can be separated by fractional distillation from the phosphoric oxychloride formed at the same time: $SO_2 + PCl_5 = SOCl_2 + POCl_3$; or still better by treating sulphur tetrachloride with sulphuric anhydride: $SCl_4 + SO_3 = SOCl_2 + Cl_2 + SO_2$; it may be purified, by distillation, from the small quantity of pyrosulphuric chloride, $S_2O_5Cl_2$, formed at the same time. In this way about 80 per cent. of the theoretical yield may be obtained. It is also formed, together with pyrosulphuric chloride, when dry chlorine free from hydrochloric acid is passed together with the vapour of sulphuric anhydride through S_2Cl_2, at 0° (32° F.), the reaction being

$$S_2Cl_2 + 3Cl_2 + 4SO_3 = 2SOCl_2 + 2S_2O_5Cl_2$$

(Michaelis, *Ann. Chem. Pharm.*, 1873, clxx. 1).

(439) **SULPHURIC DICHLORIDE,** *Sulphurylic Chloride,* or *Chlorosulphuric Acid,* $SO_2Cl_2 = 135$; *Density of Liquid,* 1·66; *of Vapour, Theoretic,* 4·61; *Observed,* 4·703; *Mol. Vol.* [⌐¬]; *Rel. wt.* 67·5; *Boiling-pt.* 77° (176°·6 F.).—If equal measures of sulphurous anhydride and chlorine, both perfectly dry, be mixed together, no change occurs in diffused daylight, but under the influence of bright sunshine they unite and become condensed to a colourless liquid, possessing an extremely pungent odour, and having an irritating effect upon the eyes. According to Melsens (*Compt. Rend.*, 1873, lxxvi. 93), chlorine and sulphurous anhydride combine, in the absence of light, if the gases are passed into glacial acetic acid. The sulphuryl chloride may be separated by fractional distillation from the chloracetic acid formed at the same time. It is said to be produced on distilling an intimate mixture of phosphoric chloride or phosphoryl chloride with plumbic sulphate; plumbic phosphate and sulphuryl chloride being formed (Carius); the reaction with the phosphoryl chloride is as follows: $3PbSO_4 + 2POCl_3 = Pb_3(PO_4)_2 + 3SO_2Cl_2$: $[3SO_2(O_2Pb)'' + 2POCl_3 = P_2O_2(O_2Pb)''_3 + 3SO_2Cl_2]$. Michaelis, however, did not succeed in preparing it by this method, the principal product being pyrosulphuric chloride, $S_2O_5Cl_2$. When sulphuric monochloride, $SO_2(OH)Cl$, is heated at about 180° (356° F.) for twelve hours, it is completely resolved into sulphuric acid and sulphurylic chloride:

$$2SO_2(OH)Cl = SO_2Cl_2 + SO_2(OH)_2$$

(Behrend, *Deut. chem. Ges. Ber.*, 1875, viii. 1004). Sulphurylic chloride is also formed on heating boric chloride with sulphuric anhydride at 120° (248° F.):

$$2BCl_3 + 4SO_3 = 3SO_2Cl_2 + B_2O_3.SO_3$$

(Gustavson, *ibid.*, 1873, vi. 9). This compound does not form salts or possess any acid properties: its relation to sulphuric acid is that of an acid chloride, both OH groups in the sulphuric acid, $SO_2(OH)_2$, being replaced by chlorine, thionylic chloride, $SOCl_2$, bearing the same relation to sulphurous acid, $SO(OH)_2$.

Sulphurylic chloride may be distilled unchanged from caustic lime or baryta; but in contact with water it is immediately decomposed into sulphuric and hydrochloric acids: $SO_2Cl_2 + 2OH_2 = H_2SO_4 + 2HCl$. It is gradually acted on by phosphoric pentachloride at the ordinary temperature with production of sulphurous dichloride, $SO_2Cl_2 + PCl_5 = SOCl_2 + Cl_2 + POCl_3$.

An analogous compound, SO_2I_2, may be obtained with iodine.

(440) **PYROSULPHURIC CHLORIDE:** $S_2O_5Cl_2 = 215$.—*Density of Liquid,* 1·819; *of Vapour,* 4·481.—This compound is formed together with phosgene, $COCl_2$, by the action of sulphuric anhydride on carbon tetrachloride: $CCl_4 + 2SO_3 = S_2O_5Cl_2 + COCl_2$. It is more conveniently prepared, however, by heating a mixture of phosphoric pentachloride and sulphuric anhydride:

$$PCl_5 + 2SO_3 = S_2O_5Cl_2 + POCl_3.$$

It may be separated from the phosphoric oxychloride by fractional distillation. Pyrosulphuric chloride is also formed by the action of sulphuric anhydride on sulphur tetrachloride or silicic tetrachloride, or by heating phosphoric oxychloride with sulphuric anhydride at 160° (320° F.): $2POCl_3 + 6SO_3 = 3S_2O_5Cl_2 + P_2O_5$. It is a colourless oily liquid of density 1·819 at 18° (64°·4 F.), and boils at 146° (294°·8 F.). It decomposes slowly in contact with water, and when heated above its boiling point is resolved into chlorine, sulphurous and sulphuric anhydrides: $S_2O_5Cl_2 = Cl_2 + SO_2 + SO_3$. This compound bears the same relation to pyrosulphuric acid, $S_2O_5(OH)_2$, that sulphuric chloride does to sulphuric acid.

(441) **SULPHUR OXYTETRACHLORIDE**, $S_2O_3Cl_4$, or $SCl_3.O.SO_2Cl$.—This substance, which was first obtained by Millon (*Ann. Chim. Phys.*, 1850, [3], xxix. 237) as a product of the action of moist chlorine on sulphur chloride saturated with chlorine, is more conveniently prepared by passing dry chlorine into a mixture of 1 mol. S_2Cl_2 with 2 mols. of sulphuric monochloride, $SO_2(OH)Cl$, cooled by a freezing mixture. The oxytetrachloride soon begins to separate in the crystalline state, when the flask should be removed from the freezing mixture and the current of chlorine continued until the product is colourless. It forms colourless crystals, which at 57° (134°·6 F.) melt and decompose, giving off chlorine and sulphurous anhydride, whilst sulphurous and pyrosulphuric chlorides remain:

$$4S_2O_3Cl_4 = S_2O_5Cl_2 + 5SOCl_2 + Cl_2 + SO_2.$$

It also decomposes when kept, even in sealed tubes, yielding a liquid which boils at 73° (163°·4 F.) and which appears to be a mixture of sulphuric and sulphurous chlorides: $S_2O_3Cl_4 = SO_2Cl_2 + SOCl_2$. It is not improbable that the oxytetrachloride may be a molecular compound of these two components. The oxytetrachloride is acted on violently by carbonic bisulphide, yielding phosgene amongst other products, the reaction being apparently:

$$7S_2O_3Cl_4 + 5CS_2 = 3COCl_2 + 6SO_2 + 2CO + 7S_2Cl_2 + 4SOCl_2:$$

in this respect it differs from all the other oxychlorides (Michaelis, *Ann. Chem. Pharm.*, 1873, clxx. 24; Michaelis and Mathias, *Deut. chem. Ges. Ber.*, 1873, vi. 1452).

(442) **SULPHURIC MONOCHLORIDE**, *Sulphuric chlorhydrate*, or *Chlorhydrosulphuric acid*, SO_3HCl, or $SO_2(OH)Cl = 116·5$.—This compound, which was first obtained by Williamson by distilling a mixture of sulphuric acid and phosphoric pentachloride, may be prepared by the direct union of hydrochloric acid and sulphuric anhydride, as when dry hydrochloric acid is passed into Nordhausen sulphuric acid. As it is apt to contain pyrosulphuric chloride, when prepared by the action of phosphoric pentachloride on sulphuric acid, if excess of the pentachloride is used, care should be taken to employ the materials in the proportions indicated by the equation:

$$3H_2SO_4 + PCl_5 = 3SO_3HCl + 2HCl + PHO_3,$$

or to act on sulphuric acid with phosphoric trichloride or oxychloride, in which case the reaction is $2H_2SO_4 + POCl_3 = 2SO_3HCl + PHO_3 + HCl$. Michaelis (*Ann. Chem. Pharm.*, 1873, clxx. 24) recommends to allow 1 mol. of phosphorous trichloride to drop slowly into 3 mols. of sulphuric acid in a flask cooled by immersing it in water, and through which a current of chlorine is passed: the trichloride is thus converted into pentachloride, and on distilling the product sulphuric monochloride is obtained. It is a colourless liquid of density 1·776 at 18° (64°·4 F.), and boils at 158°·4 (317°·1 F.). Its vapour density at 216° (420°·8 F.) was found to be 32·857 (H = 1) corresponding to about $3\frac{1}{2}$ vols. It decomposes with explosive violence when added to water,

yielding sulphuric and hydrochloric acids. Heated at 100° (212° F.) with carbonic bisulphide, it undergoes decomposition, carbonic oxysulphide, hydrochloric acid, and sulphurous anhydride being produced:

$$3SO_2(OH)Cl + CS_2 = CSO + 3HCl + 4SO_2.$$

(443) **BORIC SULPHIDE:** $B_2S_3 = 118$, $\left[\begin{Bmatrix} BS \\ S \\ BS \end{Bmatrix}\right]$ is obtained by passing the vapour of carbonic bisulphide over a mixture of carbon and boracic anhydride heated to redness:—$2B_2O_3 + 3CS_2 + 3C = 2B_2S_3 + 6CO$. It is a white solid, volatile in sulphuretted hydrogen. It is readily decomposed by water with the formation of boracic and hydrosulphuric acids:

$$B_2S_3 + 6OH_2 = 3SH_2 + 2H_3BO_3.$$

It has been suggested that boric sulphide is the source of boracic acid and sulphuretted hydrogen in the Tuscan lagoons.

(444) **NITROGEN SULPHIDE:** SN or S_2N_2; (Fordos and Gélis, *Ann. Chim. Phys.*, 1851, [3], xxxii. 389).—This compound is obtained, although only in small quantity, by passing dry ammonia through a solution of sulphur dichloride in 10 or 12 times its volume of carbonic bisulphide. The passage of the gas is continued until the brown colour of the precipitate first formed disappears; the yellow liquid is filtered from the ammonic chloride which is produced, and allowed to evaporate spontaneously, beautiful golden-yellow rhombic crystals of nitrogen sulphide mixed with crystals of sulphur are formed; the sulphur is removed by digesting the product in cold carbonic bisulphide. The reaction which takes place in the formation of this substance is very complicated and has not been completely ascertained. Nitrogen sulphide detonates powerfully by percussion, and explodes when heated to 157° (314°·6 F.). It has a faint odour, adheres strongly to paper if rubbed on it, and irritates the mucous membrane of the eyes and nose most painfully. Carbonic bisulphide takes up about $\frac{1}{300}$ of its weight when boiled with it; alcohol, ether, and oil of turpentine dissolve it very sparingly; water slowly decomposes the compound without dissolving it. Nitrogen sulphide combines with the chlorides of sulphur in several proportions.

(445) **CARBONIC BISULPHIDE,** or *Bisulphide of Carbon; Sulphocarbonic Acid,* or *Thiocarbonic Anhydride;* $CS_2 = 76$; *Density of Liquid,* 1·272 at 15°·5 (60° F.); *of Vapour, Theoretic,* 2·6296; *Observed,* 2·6447; *Mol. Vol.* $\square\square$; *Rel. wt.* 38; *Boiling-pt.* 48° (118°·4 F.).—This compound may be prepared by heating fragments of charcoal to redness in an earthen retort, into the tubulure of which is luted a porcelain tube passing nearly to the bottom of the retort: the tube is closed at its upper extremity with a cork. From time to time this cork is withdrawn, and a fragment of sulphur is dropped into the retort, the cork being immediately replaced; the sulphur melts, and is converted into vapour, which at this elevated temperature combines with the carbon, and the bisulphide thus produced may be condensed in vessels properly cooled. It is now manufactured on a very large scale, both in this country, in France, and in Germany, by the

use of suitable apparatus constructed on this principle, the vapour of sulphur being driven over red-hot coke. In order to obtain the maximum yield of bisulphide, the temperature must not be too high, as carbonic bisulphide is readily dissociated at a bright red heat, carbon being deposited and the liberated sulphur distilling over with the bisulphide. It is yellow when first formed, and contains an excess of sulphur; but by redistillation it is obtained in a state of tolerable purity. It is a very volatile, colourless liquid, of high refracting power, of an acrid, pungent taste, and possessing when impure a fœtid, peculiar, alliaceous odour. To purify it, Friedburg recommends that it should be agitated with red fuming nitric acid; after a time separated from the acid, distilled, washed thoroughly with water, and again distilled. It is heavier than water, in which it is insoluble, but it is miscible in all proportions with ether and alcohol, as well as with benzene, oil of turpentine, and the fixed and volatile oils. Bisulphide of carbon has not hitherto been frozen; hence it has sometimes been employed in the construction of thermometers destined to measure very intense degrees of cold.

The vapour of carbonic bisulphide when breathed produces great depression followed by coma. It is indeed very poisonous, and hence much care is requisite to prevent its escape into the apartments in which the workpeople are engaged. It produces in those more or less exposed to its fumes, depression, weakness, and loss of memory; for the relief of these symptoms, the use of a solution of ferrous carbonate in carbonic acid water has been found in some degree effectual. Advantage has been taken of this poisonous property to free grain infested with weevils from the insect; a small quantity of the bisulphide enclosed in an air-tight chamber with the grain, in a few hours kills both the larvæ and the eggs (Doyère), and does not injure the grain; on exposure to air the bisulphide quickly evaporates. Indeed, the applications of the bisulphide in the arts are very numerous, and of growing importance.

Carbonic bisulphide is highly inflammable and readily ignites at a comparatively low temperature, so that special precautions against fire should be taken when using it; when its vapour is mixed with hydrogen or carbonic oxide it takes fire below 215°·5 (420° F.) (Frankland). It burns with a blue flame, producing sulphurous and carbonic anhydrides. It dissolves the electronegative variety of sulphur freely, and, by spontaneous evaporation, leaves it in rhombic octohedra. Phosphorus is also freely dissolved by it, and may be obtained in crystals from the solution

by slow evaporation. Iodine, bromine, and chlorine are likewise readily dissolved by the bisulphide. It is one of the best solvents of caoutchouc, and may be substituted for ether as a solvent for some of the organic bases. It has been used on a very large scale by Deiss as a solvent for extracting oils and fats, especially in economizing the last portions of olive oil left in the pulp of the fruit after as much as possible has been obtained by pressure. It has also been used as a solvent for extracting bitumen from minerals which contain it, instead of subjecting them to the ordinary process of destructive distillation; and it has been employed as a solvent in the analysis of oil seeds, for the purpose of ascertaining the proportion of oil which the ground seeds contain (*Richardson and Watts' Technology*, vol. i. Part III., p. 138).

Carbonic bisulphide offers one of the best illustrations of the analogy in properties between oxygen and sulphur: an analogy which, although far from being so complete as that of the different halogens with each other, is yet in some respects of a striking character. It is to be remarked that sulphur is the only non-metallic element excepting oxygen with which carbon can be easily caused to unite directly. The compound of carbon and sulphur so obtained affords a good instance of the class of combinations which Berzelius has called *sulphur-acids*, these substances possessing the power of uniting with the sulphides of the basic metals, and forming with them *sulpho-salts*, corresponding in composition to analogous salts which contain oxygen. Carbonic bisulphide, for example, may be regarded as the analogue of carbonic anhydride; it contains 2 atoms of sulphur in the place of 2 atoms of oxygen, the composition of the compound being as follows:

				By weight.	By vol.
Carbon	C	=	12	or 15·79	... ?
Sulphur	S_2	=	64	84·21	... 2
Carbonic bisulphide ...	CS_2	=	76	100·00	... 2

Carbonic bisulphide combines with the sulphides of the alkali-metals, forming salts which are called *sulpho-carbonates*, such for instance as potassic sulpho-carbonate, K_2CS_3, which contains 3 atoms of sulphur in the place of the 3 atoms of oxygen in the corresponding carbonate, K_2CO_3. On boiling the aqueous solutions of the soluble sulpho-carbonates, they are easily converted into carbonates of the metal, water being decomposed, and sulphuretted hydrogen evolved, thus; $K_2CS_3 + 3OH_2 = K_2CO_3 + 3SH_2$; a similar decomposi-

tion takes place slowly in the aqueous solution at ordinary temperatures. The sulpho-carbonates, when decomposed by hydrochloric acid, form a yellow oily liquid containing the elements of carbonic bisulphide and sulphuretted hydrogen; $K_2CS_3 + 2HCl = H_2CS_3 + 2KCl$. Solutions of the sulpho-carbonates of the alkali-metals give a brown precipitate with solutions of the salts of copper: they yield, with dilute solutions of argentic nitrate and of corrosive sublimate, yellow precipitates; and with lead salts they give a red precipitate. All these precipitates blacken, more or less speedily, when kept, owing to their conversion into sulphides. Aqueous solutions of the hydrated alkalies gradually discolour the bisulphide, and form a brown liquid containing carbonate and sulpho-carbonate of the metal; $6KHO + 3CS_2 = K_2CO_3 + 2K_2CS_3 + 3OH_2$.

(446) **CARBONIC MONOSULPHIDE**, CS = 44.—Crude carbonic bisulphide exposed to sunlight deposits a brown powder, which is carbonic monosulphide. It is also produced when crude carbonic bisulphide is placed in a well-corked tube with pieces of pure iron wire, and allowed to stand for a long time. A reddish brown powder is thus formed, which consists of a mixture of ferrous sulphide and carbonic monosulphide; on treating it with hydrochloric acid, the former dissolves and leaves the monosulphide in the pure state. This substance is a maroon-coloured powder of density 1·66, insoluble in water and benzene, and only slightly soluble in boiling carbonic bisulphide and ether.

(447) **CARBON SESQUISULPHIDE**, C_2S_3, is obtained by digesting hydrogen carbosesquisulphide, $C_2S_3H_2$, with concentrated solution of ammonia at a gentle heat, and passing chlorine through the liquid; a precipitate of carbon sesquisulphide and sulphur is produced, from which the sulphur may be separated by sodic sulphite. Carbon sesquisulphide is also produced when a mixture of carbonic bisulphide and water is exposed to sunlight for some months. It is an amorphous brown powder, insoluble in alcohol, ether, and carbonic bisulphide, and readily decomposed when heated to about 200° (392° F.).

(448) **HYDROGEN CARBOSESQUISULPHIDE**, $C_2S_3H_2$, is formed when carbonic bisulphide is treated with sodium amalgam, and the product acted on with water. A red solution is thus produced, through which sulphuretted hydrogen is passed and the liquid poured into dilute hydrochloric acid, when the substance is precipitated. It is freely soluble in carbonic bisulphide, and forms salts with the metals.

(449) **CARBONIC OXYSULPHIDE**, COS, is a colourless, combustible gas of density 2·1046, produced in numerous reactions, as, for instance, when a mixture of carbonic oxide with excess of sulphur vapour is passed through a red-hot tube; and by the action of sulphuric anhydride on carbonic bisulphide, and in a much purer state by the action of sulphuric acid on potassic sulphocyanate. The oxysulphide may be purified by passing the gas into alcoholic potash, which absorbs it readily. On adding hydrochloric acid it is liberated in the pure state (Salomon, *Jour. pr. Chem.*, 1872, [2], v. 476).

(450) **NITROSULPHURIC ACID**; $H_2SO_3N_2O_2 = 142$, is not known in the form of the free acid.—Nitric oxide and sulphurous anhydride may be

mixed with each other in a dry state without entering into combination, but if a strong solution of potassic hydrate be thrown up into a jar containing a mixture of 2 volumes of nitric oxide and 1 volume of sulphurous anhydride, over mercury, the gas is gradually and completely absorbed. If a concentrated solution of ammonia be saturated with sulphurous acid, then mixed with four or five times its bulk of solution of ammonia, and a current of nitric oxide be slowly passed into the liquid whilst it is artificially kept cool, the gas is in great measure absorbed, and beautiful snow-white rhombic crystals of ammonic nitrosulphate, $(H_4N)_2SO_3N_2O_2$, are deposited; they may be collected on a filter, washed with a little ice-cold solution of ammonia, and dried *in vacuo* over sulphuric acid.

This salt is a singularly unstable compound; when dissolved in water it begins to undergo decomposition at ordinary temperatures, but the presence of a free alkali increases its stability. If an attempt be made to liberate the acid by the addition of another acid to the salt, brisk effervescence, due to the escape of nitrous oxide, takes place, and sulphuric acid remains in the liquid, $H_2SO_3N_2O_2$, giving $H_2SO_4 + N_2O$. Mere admixture of the solution of the ammonic nitrosulphate with that of many metallic salts, such for instance as cupric sulphate, produces a similar decomposition: probably a double decomposition occurs; $CuSO_4 + (H_4N)_2SO_3N_2O_2$ becoming $(H_4N)_2SO_4 + CuSO_3N_2O_2$, whilst the cupric nitrosulphate is immediately resolved into nitrous oxide and cupric sulphate. If the dry ammonic nitrosulphate be heated a little above 115° (239° F.), it is decomposed with explosive evolution of nitrous oxide.

The potassic and sodic nitrosulphates are rather more stable. No insoluble nitrosulphates have been formed; they give no precipitate with baryta-water. The nitrosulphates of the alkali-metals are neutral to test-paper, and have a pungent bitter taste.

(451) **Action of Sulphurous Acid on Nitrites**; *Sulphazotised Acids of Fremy*.—A remarkable series of salts has been described by Fremy (*Ann. Chim. Phys.*, 1845, [3], xv. 408), formed by the action of sulphurous anhydride on a solution of potassic nitrite containing a large excess of free alkali. Sulphurous anhydride combines with the elements of potassic nitrite and water in several different proportions, and forms compounds which crystallize readily, and in which neither a sulphite nor a nitrite can be detected by the usual tests. The solutions of these salts produce, in solutions of salts of barium, a precipitate which contains the new acid. These compounds are all decomposed by boiling their solutions, and ammonia and sulphuric acid are amongst the products: some of them even experience a similar decomposition at ordinary temperatures.

It is remarkable that if sodic nitrite be substituted for potassic nitrite, no sulphazotised salts are formed.

More recently these compounds have been examined by Claus, who finds that on treating a solution of potassic nitrite with an alcoholic solution of sulphurous anhydride, a very unstable salt, $SO_2.NO_2K$, is formed, which undergoes decomposition in presence of sulphurous acid and potassic hydrate, yielding numerous salts. These may be divided into three groups.

1. *Sulphammonic compounds*, in which the nitrogen is united only with hydrogen and the sulphonic group, SO_3K. Ignited with soda lime they give off the whole of their nitrogen as ammonia.

Potassic tetrasulphammonate	$NH(SO_3K)_4$
Potassic trisulphammonate	$NH_2(SO_3K)_3$
Potassic disulphammonate	$NH_3(SO_3K)_2$

2. *Sulphoxyazic compounds*, in which the hydrogen is united not only with hydrogen or the group SO_3K, but also with oxygen. Ignited with soda lime only part of the nitrogen is eliminated as ammonia.

Potassic disulphydioxyazate	...	...	$ONH(SO_3K)_2$
Potassic trisulphoxyazate	...	...	$ON(SO_3K)_3$
Potassic oxysulphazotate	...	...	$O_2N_2(SO_3K)_4$

3. *Sulphamates*, containing only trivalent nitrogen:

Potassic sulphydroxylamate	...	...	$NH(OH)(SO_3K)$
Sulphydroxylamic acid	...	...	$NH(OH)(SO_3H)$

In the formation of these compounds the sulphurous acid appears to exercise a reducing action on the nitrous acid, the reduced product combining with the SO_3K group thus formed. Most of these salts crystallize well (Claus, *Ann. Chem. Pharm.*, 1871, clviii. 52, 194; *Deut. chem. Ges. Ber.*, 1871, iv. 186, 221).

CHAPTER XII.

THE remaining halogens, bromine, iodine, and fluorine, the analogues of chlorine, may now be considered.

§ I. BROMINE: Br.=80.

Atomic Vol. of Vapour □; *Molecular Vol. of Vapour* □□; *Rel. wt.* 80; *Theoretic Density of Vapour*, 5·536; *Observed*, 5·54; *of Liquid at* 0° (32° F.) 3·18828; *Melting-pt.* −24°·5 (12°·1 F.); *Boiling-pt.* 59°·5 (139°·1 F.); *Monad as in* HBr.

(452) **BROMINE**, so named from its irritating odour (βρώμος, a stench), was discovered by Balard in the year 1826, in *bittern*, the mother-liquor of sea-water, after the less soluble salts had been extracted by crystallization. Bromine exists in sea-water in minute quantity, varying from one-third of a grain to about one grain in each gallon, or from 4 to 14 mgrms. per litre; the waters of the Dead Sea contain bromine in larger quantity than this: it appears to be combined with magnesium, as bromide of magnesium. Many saline springs, such as those of Schönebeck, Kreuznach, and Kissingen, likewise contain bromine in quantity sufficient to render its extraction from them a source of profit. It is also prepared in large quantity from the residues of the Stassfurt chlorides, and from the waters of certain springs at Ohio and elsewhere in America. Indeed, few deposits of sodic chloride exist in which traces of bromine have not been discovered. It has also been found in a silver ore from Mexico, and it is abundant in the mines of Chanarcillo, in South America; in both cases the bromide of silver is mixed with chloride of silver.

Extraction.—In order to obtain bromine, a current of chlorine

is passed into the mother-liquor from the brine, after all the salts separable by crystallization have been removed, taking care to avoid an excess of the gas, which would occasion inconvenience by forming a compound with the liberated bromine. All the soluble bromides are decomposed readily by chlorine, the attraction of chlorine for the metals being more powerful than that of bromine. In the foregoing operation magnesic chloride is formed, and bromine is set free: $MgBr_2 + Cl_2 = MgCl_2 + Br_2$; the bromine dissolving in the liquid, giving it a beautiful and characteristic yellow colour. This yellow liquid, when agitated with ether, parts with its bromine, which is dissolved by the ether, and if the mixture be placed in a glass globe closed at the top by a stopper, and furnished with a glass stopcock at the bottom, the ether rises to the surface, where it forms a beautiful golden-yellow layer. The mother-liquor is drawn off by opening the stopcock, and the ethereal solution containing the bromine is agitated with a solution of potassic hydrate; the yellow colour immediately disappears from formation of bromide and bromate of potassium which remain dissolved in the water; $3Br_2 + 6KHO = KBrO_3 + 5KBr + 3OH_2$; whilst the ether, after a time, rises to the surface deprived of its bromine, and may again be employed in a repetition of the process upon a fresh quantity of bittern. When the solution of potassic hydrate has, by repeated charges of bromine, been nearly neutralized, the liquid is evaporated to dryness, and the saline mass is gently ignited to decompose the bromate. It is then mixed with peroxide of manganese and distilled in a retort with sulphuric acid; dense red vapours of bromine pass over, which may be collected in a receiver containing water, and kept cool by ice. The decomposition is of the same nature as that attending the liberation of chlorine from sea salt by means of oxide of manganese and sulphuric acid:

$$2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2OH_2 + Br_2.$$

In this operation a small quantity of chlorine passes over with the bromine, since from the manner in which potassic bromide is formed, it is always contaminated with a portion of potassic chloride. The chlorine unites with part of the bromine, forming chloride of bromine, which is partially decomposed and dissolved by the water in the receiver, whilst the bromine is condensed in red drops. On the large scale, the mother-liquor containing the bromine as magnesic bromide is distilled in stone vessels with black oxide of manganese and dilute sulphuric acid, a current of

steam being blown in to heat the mixture, and the quantity of sulphuric acid is so adjusted that it is only just sufficient to liberate the bromine present in the solution. The bromine which distils over is collected in stoneware vessels, the vapours being absorbed by iron turnings. In order to obtain bromine free from chlorine it must be saturated with baric hydrate, which produces a mixture of bromide and chloride with bromate of barium; this mixture must be heated to redness in order to convert the bromate into bromide of barium, and the residue digested in alcohol, which dissolves nothing but the bromide. The baric bromide is obtained by the evaporation of its alcoholic solution, and when heated with black oxide of manganese and sulphuric acid it yields pure bromine. The chlorine is also removed by agitating the bromine with a solution of potassium bromide, the chlorine replacing a portion of the bromine in the latter.

In recovering bromine from residues containing alkaline bromides, or in preparing pure bromine, it is far better to employ potassic dichromate and sulphuric acid, since there is not the danger of breaking the retort, as when black oxide of manganese is used (Bolas and Groves, *Jour. Chem. Soc.*, 1871, xxiv. 784).

Properties.—Bromine is a red liquid, so deep in colour as to be nearly opaque. It has a density of 2·98 at 15° (59° F.): is very volatile, and emits dense red vapours resembling peroxide of nitrogen in colour (Part I. 2, fig. 81). In smell it resembles chlorine, and when respired, is extremely irritating to the nose and fauces, even if largely diluted with air. When swallowed, it operates as a powerfully irritating poison; it acts rapidly on all the organic tissues, and renders the skin permanently yellow. Bromine boils at 59°·5 (139°·1 F.) (Bolas and Groves); 59°·45 (Thorpe); and when exposed to a temperature of −24°·5 (−12°·1 F.) (Baumhauer) it forms a red crystalline solid. The properties of bromine greatly resemble those of chlorine, although they are less strongly developed. It bleaches many vegetable colours. Its vapour will not support the flame of a burning taper. Bromine is soluble in water to the extent of 3·6 per cent. at 5° (41° F.) and 3·226 per cent. at 15° (59°·0 F.), yielding a solution of a yellow colour; it also forms a hydrate, $Br_2.10OH_2$, crystallizing in octohedra which are not decomposed even at 15° to 20° (59° to 68° F.). The aqueous solution of bromine undergoes decomposition in sunlight, yielding hydrobromic acid and oxygen. Alcohol dissolves bromine freely, and ether still more abundantly. According to Phipson, commercial bromine sometimes contains an appreciable amount of bromide of cyanogen. Bromine com-

bines directly with phosphorus, and with some of the metals, forming compounds termed *bromides* (454), the act of combination occasionally being attended with ignition, as in the case of antimony and of tin; even gold combines with it, although slowly; its compound with silver furnishes a material of considerable value in photographic operations.

(453) **HYDROBROMIC ACID**; *Hydric Bromide* (HBr=81); *Rel. wt.* 40·5; *Theoretic Density*, 2·8026; *Observed*, 2·731; *Mol. Vol.* [ ].—Bromine resembles chlorine in its property of combining with hydrogen, forming a very powerful acid. This is a gaseous body at ordinary temperatures, consisting of equal measures of hydrogen and bromine vapour united without change of bulk. The mixture of bromine vapour and hydrogen cannot be detonated by the approach of flame, or by the electric spark, but the two elements may be made to unite slowly, by suspending a red-hot platinum wire in the mixture. If moisture be present, the formation of the acid immediately becomes apparent by the white fumes, arising from the union of the newly produced gas with the aqueous vapour.

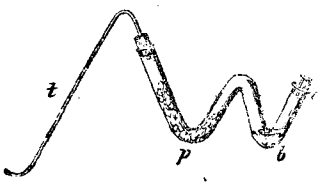
Preparation.—1. Hydrobromic acid gas may be easily obtained by decomposing potassic bromide with a concentrated solution of phosphoric acid. If sulphuric acid be used for the purpose, the product is impure, since this acid itself undergoes partial deoxidation, a mixture of hydrobromic acid, bromine, and sulphurous anhydride passing over.

2.—It may also be prepared by decomposing phosphorous bromide by means of a small quantity of water, when the following reaction occurs:

$$PBr_3 + 3OH_2 = 3HBr + H_3PO_3;$$

phosphorous and hydrobromic acids being produced. This experiment may be easily performed with the aid of a tube bent as in fig. 324. In the bend *p*, a few fragments of phosphorus and moistened glass are placed, bromine is poured into *b*, and the tube is closed by a cork, *c*; on applying a gentle heat at *b*, the bromine distils over and comes into contact with the phosphorus, forming the tri-bromide, which is decomposed by the water at the moment of its formation, and hydrobromic acid escapes by the bent tube, *t*.

FIG. 324.



3.—According to Bertrand (*Compt. Rend.*, 1876, lxxxii. 96) hydrobromic acid may be obtained by distilling calcic bromide (2 parts) with sulphuric acid (2 parts) diluted with water (1 part); under these circumstances the hydrobromic acid is not decomposed, no bromine being evolved.

Properties.—Hydrobromic acid is a colourless gas, possessing the usual irritating action of acid gases on the lungs: it is not inflammable, and extinguishes flame. Faraday succeeded in liquefying the gas under strong pressure, and in a bath of solid carbonic anhydride and ether, he even obtained it in the form of a solid, which melts at -73° ($-99^{\circ}\cdot4$ F.). The acid has the following composition.

		By weight.		By volume.
Bromine	Br =	80 or 98·76	...	1
Hydrogen	H =	1	1·24	... 1
Hydrobromic acid ...	HBr =	81	100·00	... 2

Hydrobromic acid gas is very soluble in water, forming, when concentrated, a fuming solution of greater density than hydrochloric acid. A solution of density 1·486, $HBr.5OH_2$, contains about 47 per cent. of the acid; it boils at 126° (258°·8 F.), and may be distilled without change. (See *note*, p. 246).

The following table gives the densities of aqueous hydrobromic acid according to Wright (*Jour. Chem. Soc.*, 1871, 24, 487):

Density at 15° C.	HBr in 100 parts.	Density at 15° C.	HBr in 100 parts.
1·038	5·0	1·252	30·0
1·077	10·0	1·305	35·0
1·117	15·0	1·365	40·0
1·159	20·0	1·435	45·0
1·204	25·0	1·515	50·0

Topsoë (*Deut. chem. Ges. Ber.*, 1870, iii. 403) also gives a more elaborate table of the density of solutions of hydrobromic acid, but its usefulness is diminished by the fact that the density determinations were not all made at the same temperatures.

Chlorine decomposes hydrobromic acid immediately, bromine being set free and hydrochloric acid produced. The action of hydrobromic acid upon the metallic oxides is analogous to that of hydrochloric acid, bromide of the metal and water being produced; for instance, hydrobromic acid and potassic hydrate form potassic bromide and water; $KHO + HBr$ yielding $KBr + OH_2$.

(454) **Bromides.**—The bromides are all solid at ordinary temperatures; most of them are fused by a moderate heat, and are

partially volatilized, but the bromides of gold and platinum undergo decomposition. Most of the bromides are readily soluble in water. They are all decomposed by chlorine, and when in solution may be recognized by the yellow colour of bromine which is produced by the addition of a few drops of chlorine water, taking care to avoid an excess. On agitating this yellow solution with ether, the bromine is dissolved by the ether, which on standing separates as a yellow layer of liquid, at the top of the colourless aqueous portion. If the quantity of the bromide is very minute, a small quantity of carbonic bisulphide may be advantageously substituted for ether, as it acquires a yellow tinge with an amount of bromine too small to be observed with ether; the presence of sulphuric or of sulphurous acid must however in this case be avoided. The bromides, when heated with manganic peroxide and sulphuric acid, yield red vapours of bromine; strong nitric acid has a similar effect. Hydrochloric acid decomposes the bromides at a red heat with formation of hydrobromic acid. Both argentic and plumbic nitrate give a white precipitate with solutions of the bromides, forming argentic bromide, AgBr, and plumbic bromide, $PbBr_2$, respectively; argentic bromide is insoluble in cold nitric acid, but is dissolved by a large excess of ammonia; plumbic bromide on the contrary is soluble in dilute nitric acid. Mercurous nitrate when added to solutions of the bromides gives a white precipitate of mercurous bromide, Hg_2Br_2, which is soluble in chlorine water with liberation of bromine. Cuprous bromide is only sparingly soluble. Palladium nitrate gives a black precipitate in solutions of bromides, but chlorides must be absent, otherwise no precipitate is formed.

Bromine often combines with the same metal in more than one proportion, and the compounds of bromine thus formed almost always correspond both in number and composition with the chlorides of the same metal. Oxybromides may be formed resembling the oxychlorides; and the bromides of the alkali-metals form double bromides with the bromides of those metals which yield acids with oxygen.

(455) **BROMIC ACID**; *Hydric bromate;* $HBrO_3 = 129, \left[\begin{matrix}OBr \\ O(OH)\end{matrix}\right]$.—The oxyacids of bromine are, with the exception of bromic acid, nearly unknown, and this compound has never been obtained in the form of anhydride. The bromic corresponds to chloric acid in composition. Potassic bromate is formed, together with potassic bromide, when potassic hydrate is acted on by bromine, and the acid may be obtained from the bromate, and by a process similar to that employed in the preparation of chloric acid (360). It cannot, however, be

obtained in a pure state by this means, but must be prepared by decomposing argentic bromate with bromine; this argentic salt is thrown down as a slightly soluble precipitate on adding argentic nitrate to a solution of potassic bromate. Aqueous bromic acid is a strongly acid liquid which is readily decomposed, evaporation at 100° causing it to split up with evolution of oxygen and bromine vapour. By the action of heat, potassic bromate is decomposed, potassic bromide being formed, whilst oxygen is liberated. Any solid bromate, when mixed with concentrated sulphuric acid and heated, gives off red fumes of free bromine, whilst oxygen is evolved. Argentic and mercurous bromate are anhydrous and sparingly soluble: plumbic bromate retains 1 molecule of water, $Pb_2BrO_3.OH_2$; it is also only slightly soluble. When heated with hydrochloric acid these precipitates evolve free bromine. All the salts of bromic acid which have as yet been prepared are monobasic. A *hypobromous acid*, HBrO, which is very unstable, may, it is said, be formed by agitating finely powdered mercuric oxide with bromine and water. Compounds of feeble bleaching powers may also be obtained by treating bromine with solutions of the alkalies, or with milk of lime.

Perbromic Acid; *Hydric perbromate* ($HBrO_4 = 145$).—Kammerer believed that he had obtained this acid by decomposing perchloric acid by the gradual addition of bromine to its solution, but subsequent experimenters have failed to verify this observation.

(456) **Bromous Chloride**, ($BrCl_3$?), is easily obtained by passing chlorine gas into liquid bromine: it is a volatile, reddish-yellow liquid, with a very pungent irritating odour. Water dissolves it, forming a deep yellow solution possessed of considerable bleaching power.

(457) **Boric Tribromide**, $BBr_3 = 251$.—Bromine forms a compound with boron, analogous to boric chloride, which may be prepared by the direct union of its elements, or by passing bromine vapour over a heated mixture of boric anhydride and charcoal. After being rectified over mercury, it is a colourless liquid of density 2·69, which fumes strongly in the air. It boils at 90°·5 (194°·9 F.), and is decomposed by water in the same manner as the chloride.

(458) **Bromide of Nitrogen** may be obtained by digesting potassic bromide with the so-called chloride of nitrogen; it forms a detonating oily-looking liquid, resembling chloride of nitrogen in appearance and properties.

According to Schiel, a *carbonic oxydibromide*, $COBr_2$, analogous to phosgene, may be obtained by the action of bromine vapour on carbonic oxide in the sun's rays.

No bromide of sulphur has yet been obtained, the brown red liquids formerly supposed to have the composition expressed by the formulæ, S_2Br_2 and SBr_2, being merely solutions of sulphur, as has been shown by Hannay (*Jour. Chem. Soc.*, 1873, xxvi. 823; comp. Muir, *ibid.* xxviii. 845).

§ II. IODINE: I=127.

Atomic and Comb. Vol. of Vapour [ ]; *Molecular Vol.* [ ]; *Rel. wt.* 127; *Theoretic Density of Vapour*, 8·7884; *Observed*, 8·716; *Density of Solid*, 4·947; *Melting-pt.* 107° (224°·6 F.); *Boiling-pt.* 175° (347° F.); *Monad as in* HI, *rarely Triad as in* ICl_3.

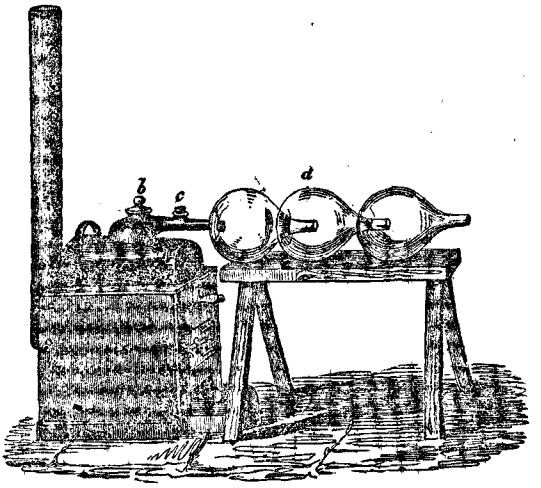
(459) **IODINE**, the third element in the group which we are now examining, is still denser than bromine, existing in the solid form at the ordinary temperature. It was accidentally discovered in the year 1811, by Courtois in the waste liquors produced in the manufacture of sodic carbonate from the ashes of sea-weed.

Iodine exists in the ocean in quantities still smaller than bromine. It is, notwithstanding, obtained with less difficulty, since the fuci, algæ, sponges, and other marine plants, extract it from sea-water, and store it up in their tissues. These, when burnt, give an ash which is technically known as *varec* or *kelp*, containing a small quantity of iodine in the form of sodic iodide. In the mineral kingdom, iodine has been found in one or two rare ores; thus it occurs combined with silver in Mexico, and with zinc in Silesia; it also exists in small quantity as iodate in the crude Peruvian sodic nitrate, and in some mineral phosphates.

Extraction.—Iodine is manufactured at Glasgow, from kelp made on the coasts of Scotland and Ireland; and also in France. The following is an outline of the process adopted in procuring it:—The sea-weed, having been dried in the sun, is burned in shallow excavations, at a low heat: owing to the volatility of the sodic iodide at a red heat, the loss of this salt would be considerable if the temperature were allowed to rise too high: in order to prevent loss of iodide by this process and also to obtain a valuable variety of charcoal and other products, Stanford proposed to distil the sea-weed in closed retorts, but chiefly owing to the difficulty of transporting the weed, the process has not been successful. The half-fused ash, or kelp, which remains, is broken into fragments and treated with boiling water; which dissolves about one-half of the ash. The liquid thus obtained is then evaporated in open pans, and all that can be separated by crystallization is removed; a double sulphate of potassium and sodium, sodic carbonate, and potassic chloride are thus extracted. The iodine

and bromine remain in the mother-liquor, which still retains disodic sulphide, besides sodic thiosulphate and some carbonate. This liquor, or *iodine ley*, of specific gravity from 1·33 to 1·38, is now mixed with one-eighth of its bulk of sulphuric acid, and allowed to stand for twenty-four hours; carbonic anhydride, sulphurous anhydride, and sulphuretted hydrogen gases escape, and sodic sulphate crystallizes out, mixed with a considerable quantity of deposited sulphur. The supernatant liquid is next transferred to a stoneware or leaden retort, which, if of lead, is of cylindrical form, *a*, fig. 325, supported in a sandbath, and gently heated from beneath by a small fire; the head of the retort, *b*, *c*, is luted on with clay, and the contents of the retort, having been heated to about 60° (140° F.), a quantity of powdered black oxide of manganese is introduced, in small portions at a time, through the tubulure, *b*. The process must be conducted slowly, at a low temperature; iodine distils over, and is condensed in the globular receivers, *d*, which are usually made of earthenware and are of considerable size. It is purified by a second sublimation. The object of the second tubulure, shown at *c*, is to facilitate the clearing of the neck of the retort in case it should become obstructed by the formation of crystals. As soon as all the iodine has come over, the retort is connected with a second condenser, more manganese dioxide is added, and the bromine distilled off and collected in a series of Woulffe's bottles. If the temperature be allowed to rise as high as 100° (212° F.) the sodic chloride retained in the ley is decomposed, chlorine is disengaged, and combines with part of the iodine, forming chloride of iodine, which causes a loss.

FIG. 325.



In the foregoing process, the addition of sulphuric acid decomposes the sodic carbonate and thiosulphate, which still

remain in solution, as well as any disodic sulphide that may be present, forming sodic sulphate which is removed by crystallization. The liquid retains an excess of sulphuric acid, and all the sodic iodide. When this mixture is heated with peroxide of manganese, the iodine is liberated, whilst hydric sodic sulphate and manganous sulphate remain in the retort. The process resembles that for chlorine or bromine:

$$2NaI + MnO_2 + 3H_2SO_4 = I_2 + 2NaHSO_4 + MnSO_4 + 2OH_2.$$

In order to obtain the iodine from the mother-liquors of 'Chili saltpetre' (sodic nitrate), in which it exists chiefly as sodic iodate, it is treated with sulphurous anhydride in quantity just sufficient to reduce the iodate; the iodine thus thrown down is then collected and sublimed. As, however, some of the iodine is present as sodic iodide, it is usually more advantageous to employ nitrous acid which decomposes both the iodate and iodide with liberation of iodine.

Commercial iodine, even when resublimed, invariably contains traces of chlorine and bromine, and also of iodide of cyanogen. It may be obtained chemically pure, however, by dissolving it in a concentrated solution of potassic iodide, and then throwing it down by diluting the filtered liquid with water; the precipitated iodine is thoroughly washed and distilled in a current of steam.

Properties.—The crystalline form of iodine is an octohedron with a rhombic base; but it is generally obtained in bluish-black scales, resembling plumbago in lustre. It is a non-conductor of electricity. At ordinary temperatures, and especially when in a moist condition, it is sensibly volatile, emitting an odour like that of chlorine, but much weaker; when heated, it fuses at 113°·6 (236°·5 F.); and boils at about 175° (347° F.), yielding a magnificent purple vapour, hence its name (from ἰοειδής, violet-coloured). According to Salet (*Compt. Rend.*, 1872, lxxiv. 1249), this vapour, when passed through a glass tube heated to a temperature just below redness, becomes self-luminous, giving off a light of a red colour. Commercial iodine often contains cyanogen iodide. Iodine, when taken internally in large doses, acts as an irritant poison: but in small quantities, it is a very valuable medicine, particularly in glandular swellings, and in certain forms of goître. It stains the skin and most organized substances of a brown colour, and gradually corrodes them. Water dissolves it in very small quantity, forming a yellow solution; one part of iodine requiring 5524 of water at 10° (50° F.) for

solution. Its bleaching properties are very feeble. Alcohol, ether, hydriodic acid, and solutions of the iodides, dissolve it freely, forming brown solutions. *Lugol's Solution*, which was formerly much used in medicine, consists of 2 parts of iodine and three of potassic iodide, dissolved in 44 parts of water; it is of a deep brown colour. Iodine is also soluble in carbonic bisulphide, to which a minute quantity imparts a beautiful rich violet colour. A strong solution of iodine in the bisulphide is opaque to light, but it allows the less refrangible heat rays to pass freely. Chloroform, carbonic tetrachloride, and benzene likewise dissolve iodine, forming red solutions. Iodine attacks many of the metals rapidly, forming *iodides;* iron or zinc is readily dissolved by it in presence of water, an iodide of the metal being formed. The compounds of iodine with hydrogen and with most of the metals are decomposed by chlorine, and even by bromine, whilst the iodine is set free: advantage is taken of this fact in ascertaining the presence of iodine. The most delicate test for it, when uncombined, is the intense blue colour which it yields with starch; by its means, with due precaution, 1 part of iodine, when dissolved in one million parts of water, may be distinctly recognized.

There are various modes of applying this test: the simplest consists in mixing a little cold starch paste with the liquid which is suspected to contain iodine; if it be present in an uncombined form, a beautiful blue colour shows itself, but if the iodine be in combination, this colour does not appear until a drop of chlorine water or of solution of bleaching powder be added to set the iodine free: an excess of chlorine must be avoided, as it forms chloride of iodine, and prevents the action of the test. David Price recommends the use of a solution of potassic nitrite as a substitute for the chlorine, the liquid to be tested being slightly acidulated; no inconvenience arises from the presence of the nitrite in slight excess. The colour fades away if the solution be heated, but is partially restored again as the temperature falls. Solutions of the alkalies, as well as of sulphurous acid, sulphuretted hydrogen, and reducing agents generally, destroy the colour. As starch paste cannot be long kept without undergoing decomposition, it is often convenient to substitute for the freshly made paste, paper which has been smeared with the starch, and allowed to become dry. If kept in a dry place, such paper may be preserved for an indefinite length of time, and is ready for use at any moment.

(460) **HYDRIODIC ACID**; *Hydric iodide,* HI=128; *Rel. wt.* 64; *Theoretic Sp. Gr.* 4·4288; *Observed,* 4·443; *Mol. Vol.* [ ].—When iodine is heated in hydrogen, the two combine in part, producing hydriodic acid; it is not, however, usually prepared in this manner. A better mode is the following:—Place in a small retort 10 parts of potassic iodide with 5 of water, and 20 of iodine; then drop in cautiously 1 part of phosphorus cut into small fragments, and apply a gentle heat. Hydriodic acid gas will be evolved abundantly, and may be collected, by displacement, in dry bottles. The iodide of phosphorus is first formed, and this is decomposed by water into hydriodic and phosphoric acids, whilst a fresh portion of hydriodic acid is liberated by the action of the phosphoric acid on the potassic iodide. The final result of the reaction is exhibited in the following equation:

$$\underset{\text{Potassic iodide.}}{8KI} + \underset{\text{Iodine.}}{10I_2} + \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Water.}}{16OH_2} = \underset{\text{Hydric dipotassic phosphate.}}{4K_2HPO_4} + \underset{\text{Hydriodic acid.}}{28HI.}$$

It may also be readily obtained by gradually adding a solution of 2 parts of iodine in 1 of a solution of hydriodic acid of density 1·7 to amorphous phosphorus contained in a retort; after allowing the mixture to stand for some time, a gentle heat is applied, when hydriodic acid is evolved in abundance.

Hydriodic acid gas is not combustible, nor does it support combustion, and when passed through a red-hot tube is partly decomposed. It fumes in the air, and possesses a powerfully acid irritating odour. It is reduced under strong pressure to a yellowish liquid which freezes at $-51°$ ($-60°$ F.). Water dissolves the gas with great avidity; the solution saturated at 0° (32° F.) having a density of 1·99 according to De Luynes.

A solution of hydriodic acid may be easily prepared by suspending iodine in water, and passing a current of sulphuretted hydrogen gas through the mixture until the brown colour of the iodine disappears; hydriodic acid is formed, and sulphur is deposited in abundance. The liquid gradually becomes clear if left at rest, and may then be decanted from the precipitated sulphur: the decomposition consists simply in the displacement of the sulphur by the iodine; $2SH_2+2I_2$ becoming $4HI+S_2$. This liquid may be concentrated until it acquires a density of 1·7, when it consists of $2HI.11OH_2$; Bineau.* It then distils

* Roscoe has shown that, both in this case and in the analogous one of the solution of hydrobromic acid (p. 239), the constancy of the boiling-point, as well as the apparent definite character of the hydrate, is accidental, and dependent upon

unchanged at 127° (260°·6 F.). The following table gives the density of aqueous solutions of hydriodic at 15° (59° F.) according to C. R. A. Wright (*Jour. Chem. Soc.*, 1871, xxiv. 655).

Density.	HI in 100 parts.	Density.	HI in 100 parts.
1·045	5	1·361	35
1·091	10	1·438	40
1·138	15	1·533	45
1·187	20	1·650	50
1·239	25	1·700	52
1·296	30		

It is a powerful acid, and dissolves iodine freely, forming a brown solution: by exposure to the air, especially if placed in a strong light, it absorbs oxygen, water is formed, and the liquid becomes brown from the liberation of iodine; if the decomposition be permitted to proceed, the iodine is ultimately deposited in fine crystals. Chlorine effects its decomposition instantaneously, whether it be in the gaseous form or in solution. Bromine and nitric acid act similarly and with almost equal rapidity; many other oxidizing agents also decompose it. Mercury decomposes it gradually, and combines with its iodine. A solution of hydriodic acid dissolves many of the metals, such as zinc and iron, with evolution of hydrogen and formation of a metallic iodide.

The composition of hydriodic acid may be ascertained by heating potassium in a measured volume of the gas. Potassic iodide is formed, and hydrogen remains equal in bulk to half the acid gas employed; consequently its decomposition may be thus represented:

			By weight.		By vol.
Iodine	I	= 127	or 99·22	...	1
Hydrogen	H	= 1	0·78	...	1
Hydriodic acid ...	HI	128	100·00		2

(461) **Iodides.**—The iodides of the metals are all solid at ordinary temperatures, and are less fusible and volatile than the corresponding chlorides and bromides. The iodides of gold, silver, platinum, and palladium are decomposed by heat into the metal and free iodine, but the greater number of the iodides are

causes similar to those traced in hydrochloric acid. (*Note*, p. 32.) Hydrofluoric acid evidently furnishes a true hydrate, but it was found to be partially decomposed by varying the temperature of evaporation.

converted into oxides when heated in the air,—the oxygen displacing the iodine. Most of the iodides are decomposed by chlorine and bromine, as well as by nitrous acid and concentrated nitric acid, with liberation of iodine. Iodine is also set free when an iodide is heated with oil of vitriol and manganic peroxide, and violet vapours of iodine are obtained. Water dissolves the greater number of the metallic iodides freely; some of them are insoluble, and exhibit colours of great brilliancy. The iodides of some of the metals which form acids with oxygen, such as those of tin, arsenic, and antimony, are decomposed by water. The soluble iodides of the metals may be obtained by the direct action of hydriodic acid upon the metallic oxide, or by the action of iodine and water upon the metal itself. These iodides, when in solution, are characterized by the reaction with starch already mentioned (459). With a solution of corrosive sublimate, $HgCl_2$, they give a beautiful salmon-coloured precipitate, which almost immediately changes to a brilliant scarlet; this is mercuric iodide: it is soluble in excess both of potassic iodide and of corrosive sublimate. Mercurous nitrate gives a green precipitate in solutions of the soluble iodides. With plumbic nitrate they yield a bright yellow precipitate of plumbic iodide, which is slightly soluble in boiling water, especially if the lead salt be present in excess; on cooling, the plumbic iodide is deposited in very beautiful lustrous golden scales. With argentic nitrate a buff-coloured argentic iodide is formed, which is nearly insoluble in ammonia, but freely soluble in sodic thiosulphate and in potassic cyanide. If a mixture of ferrous sulphate and cupric sulphate be added to a solution of any iodide, a white precipitate of cuprous iodide, Cu_2I_2, is obtained. With auric chloride the iodides give a lemon-yellow precipitate; and with salts of palladium a brown palladious iodide, PdI_2, is produced, which is sometimes used for determining the quantity of iodine present in a solution in which it occurs mixed with chlorine, since palladious chloride is freely soluble in water.

(462) **CHLORIDES OF IODINE.**—Two compounds of iodine with chlorine, a protochloride, ICl, and a trichloride, ICl_3, are known.

The *protochloride*, or *iodous chloride*, ICl, as obtained by distilling 1 part of iodine with 4 parts of potassic chlorate, is a very irritating, volatile, yellowish-brown liquid, which solidifies, on standing, to a mass of dark lustrous crystals, of density 3·1822 at 0° (32° F.), having the appearance of iodine; it melts at 24°·2 (75°·6 F.), and boils at 101°·3 (214°·5 F.); it dissolves, apparently

without change, in alcohol, and in ether. On adding iodine protochloride to water it is partly decomposed, iodine being precipitated, and hydrochloric and iodic acids formed, which remain in solution:

$$10ICl + 6OH_2 = 4I_2 + 10HCl + H_2I_2O_6.$$

The hydrochloric acid thus produced dissolves a portion of unchanged protochloride, the latter being soluble without decomposition in hydrochloric acid of density 1·100. This chloride when hot dissolves iodine readily, and deposits it in beautiful crystals.

Trichloride of iodine, or *iodous trichloride*, ICl_3, is prepared by treating iodine with excess of dry chlorine gas, or by acting on pure dry hydriodic acid with chlorine, taking care to keep the latter in excess, when it is obtained in golden-yellow crystalline scales quite free from iodine, $HI + 2Cl_2 = ICl_3 + HCl$. If the hydriodic in acid is in excess, the trichloride becomes converted into the monochloride, $ICl_3 + HI = 2ICl + HCl$ (Christomanos, *Deut. chem. Ges. Ber.*, 1877, x. 434). When heated in air it does not fuse, but splits up into chlorine and the monochloride; in an atmosphere of chlorine, however, it melts unchanged at 33° (91°·4 F.), but at 77° (170°·6 F.) even under these circumstances, it is completely resolved into chlorine and the monochloride. Its vapour is extremely irritating to the eyes. The trichloride acts on carbonic bisulphide at the ordinary temperature forming a reddish-brown liquid, which contains sulphur chloride, carbon tetrachloride, and a crystalline substance having the composition, $ICl_3.SCl_4$: this may be readily prepared by saturating a solution of iodine in carbon bisulphide with chlorine; heat is developed, and as the liquid cools the new compound separates in the crystalline state. It may also be formed by passing chlorine over a mixture of sulphur and iodine in molecular proportions. It attracts moisture when exposed to the air, and dissolves in water, apparently without decomposition. Alkaline solutions decompose it, and iodine is precipitated as in Liebig's method of preparing iodic acid (464).

Bromides of Iodine.—Iodine also combines with bromine, and forms compounds with it which are possessed of properties similar to those of the chlorides of iodine.

(463) **OXIDES OF IODINE.**—Iodine has a more powerful attraction for oxygen than either chlorine or bromine, and forms with it two compounds which by their action upon water furnish well-defined acids, viz., iodic acid, $H_2I_2O_6$, and periodic acid, H_5IO_6, besides some other oxides but imperfectly known.

Iodic Anhydride; $I_2O_5=334$, [I-O-O-O-O-O-I]; *Comp. in* 100 *parts*; I 76·04; O 23·96.—This body may be obtained by cautiously heating iodic acid at 170° (338° F.). It is a white powder, easily soluble in water, and has a density of 4·487 at 0° (32° F.).

(464) **IODIC ACID**; *Hydric iodate*, $H_2I_2O_6=352$.—This acid is often regarded as corresponding in composition to chloric and bromic acids. It may be prepared in several ways.

1.—It may be procured by boiling iodine in concentrated nitric acid for a long time.

2.—Equal parts of potassic chlorate and iodine may be mixed with 5 parts of water and a little nitric acid: chlorine is thus evolved in abundance, whilst potassic iodate is formed and dissolved in the liquid: the chloric acid which is set free in the first instance by the nitric acid imparts its oxygen to the iodine, chlorine gas escaping, whilst the iodic acid liberates a fresh portion of chloric acid from the chlorate, and this undergoes a similar decomposition (Millon).

3.—Iodine is suspended in water, containing potassium chlorate in the proportion of 122·5 parts for each 127 of iodine, and chlorine is passed in. On warming the liquid, chlorine is evolved and potassium iodate is formed: $2KClO_3+2ICl=K_2I_2O_6+2Cl_2$. The iodate crystallizes out as the solution cools (Henry, *Deut. chem. Ges. Ber.*, 1870, iii. 892).

4.—Liebig's plan of preparing iodic acid consists in suspending iodine in water, and passing a current of chlorine gas through it until the iodine is dissolved; the liquid is then neutralized by sodic carbonate, which causes an effervescence, attended by a precipitation of iodine, which may be again dissolved by passing chlorine through the liquid, repeating the series of operations until all the iodine is converted into iodic acid. In this case the chlorine combines directly with the iodine and forms trichloride of iodine, which is dissolved by water unaltered: it is decomposed on the addition of the alkaline carbonate in the following manner:

$$\underset{\text{Trichloride of iodine.}}{10ICl_3} + \underset{\text{Sodic carbonate.}}{18Na_2CO_3} = \underset{\text{Sodic chloride}}{30NaCl} + \underset{\text{Sodic iodate.}}{3Na_2I_2O_6} + \underset{\text{Iodine.}}{2I_2} + \underset{\text{Carbonic anhydride.}}{18CO_2}.$$

The neutralized liquid contains sodic iodate and chloride. Baric chloride is next added; an abundant precipitate of the sparingly soluble baric iodate is formed, which is washed so as to free it from adhering salts, and is then decomposed by a quantity of sulphuric acid just sufficient to combine with the barium: the

iodic acid is dissolved by the water, and may be separated from the insoluble baric sulphate by filtration.

5.—On mixing solutions of calcic hypochlorite and potassium iodide, calcic iodate is formed and crystallizes out, and by evaporating the mother-liquors a further quantity may be obtained. Iodic acid is easily prepared from this salt by decomposing it with the requisite quantity of dilute sulphuric acid, and evaporating the solution, after separation of the calcic sulphate by filtration.

Iodic acid may be obtained by spontaneous evaporation of its aqueous solution in crystals composed of $H_2I_2O_6$: when heated it loses water, but from Ditte's observations (*Ann. Chim. Phys.*, 1870, [4], xxi. 5) on the vapour tension at various temperatures it has been shown that no other definite hydrate exists; on raising the heat to 170° (338° F.), it is converted into the anhydride, and at about 371° (700° F.), it is decomposed into iodine and oxygen. Its solution is destitute of odour, and has a sour, astringent taste: many organic bodies decompose it, and owing to this circumstance litmus-paper is first reddened and afterwards bleached by it.

Iodates.—From Thomsen's researches, iodic acid appears to be dibasic, and differs greatly from chloric and bromic acids, inasmuch as most of its salts dissolve with difficulty, and it readily yields the anhydride when heated; moreover, it forms acid salts with the alkali-metals; in these respects it resembles the polybasic acids. The thermic phenomena of the formation of iodic acid from its elements also strongly supports this view (Thomsen, *Deut. chem. Ges. Ber.*, 1873, vii. 112). Several potassic iodates are known: $K_2I_2O_6$, the normal iodate, which crystallizes anhydrous from its aqueous solution; from dilute sulphuric acid, however, it separates as $K_2I_2O_6.OH_2$. The diiodate, $K_2I_2O_6.H_2I_2O_6$, is deposited on cooling from a solution of the normal iodate in boiling nitric acid diluted with an equal volume of water. The triiodate, $K_2I_2O_6.2H_2I_2O_6$, is formed from the normal iodate with a large excess of iodic acid; it loses two molecules of water when heated at 150°—200° (302°—392° F.), becoming $K_2I_2O_6.2I_2O_5$. All the iodates are decomposed by heat: if the metal have a stronger attraction for iodine than for oxygen, an iodide of the metal is formed and oxygen is evolved; for instance, potassic iodate, $K_2I_2O_6$, becomes $2KI + 3O_2$: but if the attraction of the metal be greater for oxygen than for iodine, an oxide is left behind: baric iodate, for example, is converted into baryta, oxygen gas, and free iodine, the violet vapours of the latter

escaping along with the oxygen; $2BaI_2O_6$ yielding $2BaO + 5O_2 + 2I_2$. The iodates of the metals of the alkaline earths, if not heated too strongly, leave a basic periodate, the barium salt consisting of $BaI_2O_8.4BaO$. The aqueous solutions of the iodates are decomposed by sulphurous acid; for example, $K_2I_2O_6 + 6H_2SO_3 = 2KI + 6H_2SO_4$; an iodide of the metal is formed, and then the iodine may be detected by the starch test in the usual way. With the exception of the iodates of the alkali-metals, the iodates are but sparingly soluble. The calcium salt retains $6OH_2$; those of strontium and barium, $BaI_2O_6.OH_2$, if precipitated from hot solutions, retain OH_2; whilst the iodates of lead and silver are anhydrous. Argentic iodate is insoluble in dilute nitric acid.

(465) **PERIODIC ACID**; *Hydric periodate;* H_5IO_6 or $H_2.IO_6H_3$ = 228.—This acid differs from perchloric acid in the same way that iodic acid differs from chloric acid. It is dibasic and pentatomic, the relation between it and iodic acid being expressed by the formula:

	$H_2IO_6.I$	$H_2IO_6.H_3$
or	$(OH)_2IO(IO_3)$	$(OH)_2IO(OH)_3$
	Iodic acid.	Periodic acid.

The atom of iodine in iodic acid being replaced by three atoms of hydrogen. This formula for periodic acid agrees with Thomsen's results on the heat of neutralization of periodic acid, and with the molecular volumes of the solutions of the two acids. Periodic acid is obtained by passing a current of chlorine gas through a solution of sodic iodate to which sodic hydrate has been added in the proportion of 3 molecules of free alkali to 1 molecule of sodic iodate: an unusual decomposition takes place, giving rise to a sparingly soluble sodic periodate. The reaction which occurs may be represented as follows:

$Na_2I_2O_6$	+	$6NaHO$	+	$2Cl_2$	=	$2Na_2IO_6.H_3$	+	$4NaCl$.
Sodic iodate.		Sodic hydrate.		Chlorine.		Sodic periodate.		Sodic chloride.

The sodic periodate, $Na_2IO_6.H_3$, is dissolved in dilute nitric acid, and precipitated by argentic nitrate; the argentic periodate thus produced is then dissolved in boiling nitric acid; an acid argentic periodate, $Ag_2IO_6.H_3$, crystallizes as the liquid cools, and this salt when treated with water is decomposed into a basic argentic periodate, which is insoluble, and periodic acid, which is dissolved. By evaporating the solution, the periodic acid may be obtained in deliquescent oblique rhombic prisms, $H_2IO_6.H_3$, which are somewhat soluble in alcohol and in ether. It melts at 133° (271°·4 F.), and at 140° (284° F.) is completely decomposed, yielding iodic anhydride, oxygen, and water. The periodates are most of them sparingly soluble in water, but are dissolved freely by dilute nitric acid. Periodic acid contains 5 atoms of hydrogen in the molecule of which two are basic, but salts are known containing 1, 2, 3, 4, and 5 atoms of a univalent metal respectively. The sodic salt, $NaHIO_6.H_3 + OH_2$, is obtained on dissolving the normal salt, $Na_2IO_6.H_3$, in hot nitric acid, and allowing it to cool. On adding argentic nitrate to a neutral or slightly acid solution of sodic periodate, an almost black precipitate of basic argentic periodate, Ag_5IO_6, is produced. When this salt is dissolved in hot nitric acid, the solution on cooling deposits normal argentic periodate, $Ag_2IO_6.H_3$, in straw-yellow rhombohedral crystals. A solution of periodic acid when nearly neutralized with calcic carbonate and

evaporated, deposits crystals of calcic periodate, $CaIO_6.H_8 + 3OH_2$, and the strontic salt, $SrIO_6.H_8 + OH_2$, may be obtained in a similar way. The baric salt, $BaIO_6.H_8 + 2OH_2$, which is only sparingly soluble, is precipitated on mixing a solution of a baric salt with an alkaline periodate. Numerous other salts of periodic acid containing various proportions of metal are known.

The periodates are decomposed by hydrochloric acid with evolution of chlorine, and by hydric sulphide with separation of sulphur. Sulphurous anhydride causes a precipitate of iodine in their solutions, which with excess redissolves as hydriodic acid. The most characteristic reaction of periodic acid is the formation of mercurous periodate on adding a solution of mercurous nitrate to a solution of a periodate; it is a yellow precipitate which becomes converted into the green mercurous iodide on treatment with stannous chloride.

(466) **IODIDE OF NITROGEN.**—By digesting iodine for half an hour in a cold solution of ammonia, a black powder is obtained. The brown supernatant liquid, which contains an excess of iodine held in solution by ammonic iodide, is decanted, and the insoluble powder is placed upon filtering-paper in quantities of a grain or less, and allowed to dry spontaneously. Two compounds (NI_3 and NHI_2) appear to be formed together under these circumstances; both these compounds, when dry, explode upon the slightest touch, and indeed often detonate without any assignable cause: the explosion is remarkably sharp and sudden; fumes of iodine are produced, and a faint light is emitted.

Stahlschmidt finds that in order to obtain the compound NHI_2 in a state of purity, a cold saturated solution of iodine in absolute alcohol should be mixed with twice or thrice its bulk of a saturated solution of ammonia in absolute alcohol; the precipitate thus formed must be washed with absolute alcohol. If the alcoholic solution of iodine be precipitated with concentrated aqueous solution of ammonia, and the precipitate washed with water, the black powder consists of a body which may be represented by the formula NI_3, or ammonia in which the 3 atoms of hydrogen have been displaced by 3 of iodine.

Iodide of nitrogen becomes slowly decomposed in water; ammonia retards, but potassic hydrate and the acids accelerate the decomposition; chlorine and bromine cause it to explode, whilst strong nitric acid destroys it rapidly; sulphuretted hydrogen also decomposes it, quietly but completely. The results of the reaction last mentioned afford a means of ascertaining the relative quantities of nitrogen and iodine contained in the body under examination: 1 molecule of the black powder, NHI_2, when treated with 2 molecules of sulphuretted hydrogen, furnishes 1 molecule of ammonic iodide, 1 of hydriodic acid, and 2 atoms of sulphur:

$$NHI_2 + 2SH_2 = NH_4I + HI + S_2.$$

(467) **Iodide of Sulphur**, S_2I_2, is a crystalline brittle steel-grey solid; but the compound is unstable, gradually losing iodine on exposure to the air.

A *Sulphuryl Iodide*, SO_2I_2, analogous to sulphuryl chloride, has been obtained.

(468) **Natural Relations of the Halogens.**—It is impossible not to be struck with the close analogy presented by the three elementary bodies, chlorine, bromine, and iodine, both in their uncombined state and in their compounds: they indeed form one of the best defined natural groups of simple substances. All these elements possess the characteristic property of combining with hydrogen in the proportion of 1 volume of the gas or vapour to 1 volume of hydrogen; the union occurring without change of bulk, and the compound formed being powerfully acid, and extremely soluble in water. Chlorine, bromine, and iodine are also capable of displacing hydrogen from many organic compounds, producing substances which correspond in composition with the original body, but in which a certain number of atoms of the halogen have taken the place of a corresponding number of atoms of hydrogen.

The specific gravity, fusing-point, and boiling-point of these elements rise as the atomic weight increases, as is shown in the table which follows:

Elements.	Density.		Melting point.		Boiling point.		Atomic weight.	Diff. between at. weights.
	Gaseous.	Liquid or solid.	°C.	°F.	°C.	°F.		
Fluorine	1·313?	?		?		?	19	
Chlorine	2·47	1·33		?		?	35·5	16·5
Bromine	5·54	3·1883	— 24·5	— 12·1	59·5	139·1	80·0	44·5
Iodine	8·7884	4·947	113·6	236·5	175	347·0	127·0	47·0

The intensity of their chemical activity usually decreases as the combining number increases, but this is not invariably the case, for some metals, silver and mercury, for instance, appear to have a stronger affinity for iodine than for bromine or chlorine at ordinary temperatures, mercuric bromide or chloride and argentic chloride being completely converted into the corresponding iodide by treatment with concentrated hydriodic acid at the ordinary temperature. The probable explanation of this apparent anomaly will be noticed in the chapter on thermo-chemistry. At ordinary temperatures, chlorine is gaseous, bromine liquid, iodine solid; the properties of bromine being indeed intermediate between those of chlorine and iodine. When in the liquid form,

the three elements have the same atomic volume; and when united with the same metal the salts which they furnish are isomorphous; potassic chloride, bromide, and iodide, for example, all crystallize in cubes. Each of these elements also forms powerful acids with oxygen.* The attraction of these three halogens for oxygen is, however, in the inverse order of that of the same halogens for hydrogen and the metals. Neither iodic anhydride, nor the acid in solution, is decomposed by free chlorine or bromine: bromic acid and the bromates are also unaffected by free chlorine: but iodic acid is easily obtained by the decomposition of chloric or bromic acid by free iodine.

At the time that iodine was discovered, chlorine was by most chemists regarded as a compound of muriatic acid and oxygen, and was consequently known as *oxymuriatic acid.* Indeed, many of the reactions which it presented admitted of a simple explanation on this hypothesis, and this circumstance prevented chemists from adopting generally the views which had a short time previously been put forward by Davy, maintaining the elementary nature of chlorine. The discovery of iodine, however, decided them, and assisted materially in fixing the opinion now entertained respecting the compounds of fluorine, the fourth member of the group, but of which our knowledge is in a much less satisfactory condition.

§ III. FLUORINE: F=19.

Theoretical Density, 1·315; *Theoretical Comb. Vol.* [ ]; *Rel. wt.* 19; *Monad, as in* HF.

(469) MANY unsuccessful attempts have been made at various times to isolate fluorine. Its chemical activity is so powerful, and its action on the human frame is so irritating and deleterious, that scarcely anything is known concerning it in its free state. No doubt, however, is entertained of its general nature, since its compounds are closely analogous to the corresponding ones of the three elements of the haloid group which have been already described.

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* Nitrogen is remotely connected with this group by the analogy between the nitrates and the chlorates, and between the nitrites and the chlorites; in the natural grouping of the elements, it forms an intermediate link between the halogens and the elements, belonging to the phosphorus family; its compound with hydrogen (viz., ammonia) presenting many analogies with phosphuretted hydrogen, whilst the analogies between the derivatives of ammonia and of phosphuretted hydrogen are very striking, as will be more fully shown hereafter.

According to Kammerer (*Chem. Centr.*, 1862, p. 523), when argentic fluoride in excess is heated at 70°—80° (158°—176° F.) with iodine in a glass tube free from air for 24 hours, a colourless gas is produced, which does not attack glass, is permanent over mercury, and is rapidly absorbed by a solution of potassic hydrate. Gore (*Phil. Trans.*, 1870, 239, and 1871, 321; also *Proc. Roy. Soc.*, 1871, xix. 235, and xx. 70), however, finds that iodine slowly displaces fluorine from dry, argentic fluoride at temperatures of 93°·3—260° (200°—500° F.), and forms a loosely combined compound of fluorine, argentic iodide, and iodine. This when heated strongly yields iodine fluoride, and not free fluorine. Attempts to obtain fluorine by the decomposition of dry argentic fluoride by bromine and chlorine were equally unsuccessful.

Fluor-spar, or calcic fluoride, CaF_2, is with the exception of cryolite, $6NaF.Al_2F_6$, the only compound of fluorine which exists abundantly in nature, and from it, all the preparations of fluorine are obtained. Small quantities of calcic fluoride are contained in a variety of minerals, particularly in the phosphates of calcium and certain kinds of mica. It exists too in minute quantity in the bones of animals, and especially in the teeth.

(470) **HYDROFLUORIC ACID**; *Hydric fluoride*, HF=20; *Rel. wt.* 10; *Theoretic Density of anhydrous Vapour*, 0·692; *Atomic Vol.* [ ].—No compound of fluorine with oxygen is known, but in union with hydrogen it forms a very remarkable acid.

Preparation.—In order to procure hydrofluoric acid in solution in a concentrated form, 1 part of finely-powdered fluor-spar, free from silica and the metallic sulphides, is mixed with 2 or 3 parts of oil of vitriol; at ordinary temperatures no evolution of vapour occurs if the fluor-spar be pure, but a transparent gelatinous mass is formed. On the application of a gentle heat dense acid fumes of an extremely deleterious nature arise, and a reaction takes place similar to that which occurs in the preparation of hydrochloric acid:

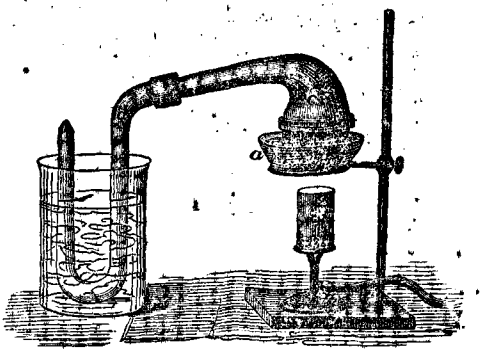
$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

Owing to the powerfully corrosive action exerted by hydrofluoric acid upon glass, which it deprives of its silicon, it is necessary always to prepare it in metallic vessels. For ordinary purposes, the distillation may be conducted in a leaden retort. For the convenience of removing the charge after the operation is over, it is found advantageous to make the retort in two pieces; a head and a body; the head, *c*, fig. 326, fits accurately by an overlapping grooved joint into the body, *b*. The heat may be conveniently applied in an equable manner by placing the body of the retort in a shallow iron tray, *a*, filled with sand: *d* is the receiver for the acid: it consists of a leaden pipe fitted by grinding to the neck of the retort, and is cooled by immersion

in a mixture of ice and salt. When a perfectly pure acid is required, the still and receiver should be of platinum.

The concentrated acid obtained by the foregoing method was long believed to be anhydrous; but the researches of Louyet (*Compt. Rend.*, 1847, xxiv. 434) have proved that it contains water. He distilled it with an excess of phosphoric anhydride: the water was thereby removed, and a colourless gas of an extremely irritating nature was set free; it produced dense fumes on escaping into the air, had but little action on perfectly dry glass, and was rapidly condensed by water. Fremy (*Ann. Chim. Phys.*, 1856, [3], xlvii. 7) prefers to subject the double fluoride of potassium and hydrogen, KF.HF, to distillation; the salt is first rendered anhydrous by careful desiccation, and on afterwards applying a strong heat, the equivalent of hydrofluoric acid is expelled: by the application of a freezing mixture of ice and salt, the anhydrous acid is obtained in the form of a colourless, mobile, very volatile liquid. Fremy also obtained the anhydrous acid by decomposing plumbic fluoride by dry hydrogen.

FIG. 326.



Properties.—Both the anhydrous acid and its aqueous solution have been very carefully examined by Gore (*Phil. Trans.*, 1869, p. 173). He finds that anhydrous hydrofluoric acid is a colourless mobile liquid of density 0·9879 at 12°·8 (55° F.), which boils at 19°·4 (67° F.), and does not solidify at −34°·5 (−30° F.); its vapour tension at 15°·5 (60° F.) is equal to 7·58 pounds per square inch. The gaseous acid when quite dry does not attack glass even when left in contact with it for weeks. The acid obtained by distilling fluor-spar with oil of vitriol is a densely fuming, volatile, colourless liquid, which boils at about 16° (60°·8 F.), and remains unfrozen at −20° (−4° F.). The preparation of this acid should be conducted with the greatest care, and special provision must be made for carrying off the fumes from the operator. The liquid acid is highly dangerous, from its caustic action upon the skin, the smallest drop occasioning a deep and painful burn. Indeed, it ought never to be preserved in the concentrated form.

When poured into water it combines with it with great avidity, and with the evolution of so high a temperature as to produce a hissing noise, resembling that caused by quenching a red-hot iron. Although the anhydrous acid has a specific gravity of 0·988, by the addition of water the density may be increased to about 1·250, beyond which point further dilution is attended with a regular decrease in density. The acid of density 1·150, $HF.2OH_2$, boils at 120° (248° F.), and may be distilled unchanged. (See *note*, p. 247.) Dilute hydrofluoric acid gradually dissolves the metals, excepting platinum and some of the metals associated with it, and gold, silver, lead, and mercury; the metal whilst undergoing solution displaces hydrogen. On this account and as it also attacks glass, the acid must be kept in platinum vessels if concentrated; the dilute acid may be stored in leaden vessels, or more conveniently in bottles made of gutta-percha. Potassium, if thrown into the strong acid, decomposes it with explosion.

Tests.—Hydrofluoric acid is easily recognized by its corrosive action upon glass. In order to detect a fluoride in a compound which is suspected to contain it, the material is reduced to a fine powder and mixed in a platinum capsule with strong sulphuric acid; a slip of glass is warmed and rubbed over with beeswax so as to coat it uniformly; a few characters are next traced with a point through the wax, so as to expose a portion of the glass: this etching is then inverted over the platinum capsule, which is gently warmed for a few minutes, the glass being cooled with a piece of moistened filtering paper, in order to prevent the wax from becoming melted. If fluorine be contained in the mixture, the glass, on cleaning off the wax with a little oil of turpentine, will be found to be corroded in the parts exposed: if the traces be very faint, they may be rendered visible by breathing upon the surface of the plate.

A weak solution of hydrofluoric acid is often employed advantageously for etching on glass; in this way, for instance, the graduations on the glass stem of a thermometer may be made with great precision and facility; the glass tube is first coated with engravers' etching varnish, the divisions are traced through the varnish with a fine point, and the tube is plunged into a long leaden tube filled with the dilute acid; in the course of a few minutes the scale is permanently engraved: when the engraving is effected by the vapour of the acid, the traces are white and opaque, but if the liquid acid be used the lines are transparent.

(471) **Fluorides.**—Most of the compounds of the metals with fluorine fuse easily on the application of heat, and hence the origin of the terms *fluor*-spar and fluorine (from *fluo*, to flow). When ignited in a current of steam, many of them are converted into the corresponding oxides, whilst hydrofluoric acid is formed. Stannous and argentic fluorides are easily soluble in water, but those of potassium, sodium, and iron are only sparingly soluble; the other fluorides are insoluble, or only very sparingly soluble, in water. They are all decomposed when heated with oil of vitriol, and evolve hydrofluoric acid, but they are not so readily attacked by nitric acid. If heated in a current of chlorine, all the fluorides are decomposed, whilst chlorides of the metal are produced. The solutions of the soluble fluorides corrode the glass vessels in which they are contained: they give no precipitate with argentic nitrate, since argentic fluoride is soluble: but with salts of lead, barium, magnesium, and calcium, insoluble precipitates are produced, consisting of the fluorides of these metals. Calcic fluoride is so transparent as to be perceived with difficulty; but on heating the liquid, or on the addition of ammonia, it is rendered more opaque.

Many metallic fluorides combine with an additional atom of hydrofluoric acid, and form compounds which may often be obtained in crystals that are soluble in water. The double fluoride of potassium and hydrogen, KF.HF, has been already mentioned as a convenient source for preparing anhydrous hydrofluoric acid. Double fluorides of the alkali-metals with the fluorides of the electronegative metals which form acids with oxygen may likewise be obtained with facility. They are analogous to the double fluoride of hydrogen and potassium just mentioned:

Potassic hydrofluoride	KHF_2	or KF.HF
Potassic borofluoride	KBF_4	$KF.BF_3$
Potassic silicofluoride	K_2SiF_6	$2KF.SiF_4$
Potassic stannofluoride	K_2SnF_6	$2KF.SnF_4$
Potassic titanofluoride	K_2TiF_6	$2KF.TiF_4$
Potassic zircofluoride	K_2ZrF_6	$2KF.ZrF_4$

Many insoluble metallic anhydrides, such as tantalic, titanic, molybdic, and tungstic anhydrides, are dissolved by hydrofluoric acid, fluorides of the metals being formed, whilst the oxygen of these compounds produces water with the hydrogen of the hydrofluoric acid: the metallic fluorides so formed are dissolved by the excess of hydrofluoric acid, and give rise to new compound acids. Titanic anhydride, for instance, is thus converted into fluotitanic acid; TiO_2+6HF becoming $2HF.TiF_4+2OH_2$. Silica yields a

similar compound, $2HF.SiF_4$. The fluorides of antimony, arsenicum, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc are volatile without decomposition.

Hydrofluoric acid, when mixed with nitric acid, readily dissolves silicon which has not been strongly ignited; but it is remarkable that the mixture does not dissolve either gold or platinum.

Numerous other compounds of fluorine have been prepared, but they are not of sufficient practical importance to require notice here: the compounds which it forms with silicon will be described hereafter (487).

(472) **FLUORIC IODIDE**, FI_5.—Gore (*Proc. Roy. Soc.*, 1871, xix. 235), on heating argentic fluoride with iodine in a platinum vessel, obtained besides argentic iodide and a double salt of argentic iodide and platinic fluoride, a colourless liquid of high boiling point, which does not attack platinum even at a red heat; it acts on glass, however, at 15°·5 (60° F.), and is decomposed by water with violence, yielding hydrofluoric and iodic acids:

$$2IF_5 + 6OH_2 = 10HF + H_2I_2O_6.$$

(473) **BORIC FLUORIDE**, or *Trifluoride of boron*, $BF_3=68·0$; *Rel. wt.* 34·0; *Theoretic Density*, 2·353; *Observed*, 2·372; *Mol. vol.* [ ].—Boron forms with fluorine a body analogous to boric chloride. It may be prepared in the following manner: 2 parts of fluor-spar and 1 of fused boracic anhydride, both in fine powder, are intimately mixed, and intensely ignited in a wrought-iron tube closed at one end; decomposition occurs according to the equation:

$$\underset{\text{Calcic fluoride.}}{3CaF_2} + \underset{\text{Boric anhydride.}}{4B_2O_3} = \underset{\text{Calcic borate.}}{3(Ca_2BO_2)} + \underset{\text{Boric fluoride.}}{2BF_3}.$$

$$\left[3CaF_2 + 4 \begin{Bmatrix} BO \\ O \\ BO \end{Bmatrix} = 3 \begin{matrix} BO \\ BO \end{matrix} (O_2Ca)'' + 2BF_3. \right].$$

Calcic borate remains in the tube, and the boric fluoride passes off as a colourless gas which may be collected over mercury. A very convenient way also is to distil a mixture of calcic fluoride, boric anhydride, and sulphuric acid in a platinum retort. The composition of the boric fluoride is the following:

		By weight.		By vol.
Boron	B ...	11·0 or	16·18 ...	1
Flourine ...	F_3 ...	57·0	83·82 ...	3
		68·0	100·00	2

Boric fluoride does not support combustion; it has an irritating odour, and fumes densely in the air. It is rapidly absorbed

by water, which at 0° (32° F.) absorbs 1057 times its volume of the gas with considerable rise of temperature, forming a fuming oily acid liquid, which is very corrosive, charring organic matter as powerfully as oil of vitriol. This solution has been called *borofluoric acid,* but Basarow (*Compt. Rend.*, 1874, lxxviii. 1689, and lxxix. 483) has found that it is merely a solution of boric fluoride in water which has undergone partial decomposition into boric acid and hydrofluoboric acid. This solution has no constant boiling-point, for when heated, boric fluoride is given off copiously at 140° (284° F.), and at about 160°—170° (320°—338° F.) a very viscid liquid distils over, which has a density of 1·727, and fumes strongly on exposure to the air; the subsequent fractions boil at higher temperatures up to 200° (392° F.).

When the solution of boric fluoride is largely diluted with water, one-fourth of the boron is separated in the form of boric acid, and another compound is found in solution termed *hydrofluoboric acid.* This acid appears to consist of a molecular compound of hydrofluoric acid with boric fluoride, and is formed in the following manner:

$$4BF_3 + 2OH_2 = HBO_2 + 3HF.BF_3.$$

So strong is the tendency to the formation of this compound in dilute solutions, that if boric acid be added to a solution of potassic or ammonic fluoride, for each molecule of boric acid, three of potassic or ammonic hydrate are liberated and a borofluoride produced:

$$4KF + HBO_2 + OH_2 = KF.BF_3 + 3KHO.$$

(474) **FLUORIDE OF CARBON.**—When argentic fluoride is heated with chlorine in a carbon boat, or when the vapour of carbonic bisulphide is passed over the fluoride at a red heat, a gaseous compound of fluorine and carbon, CF_4, is produced, the reaction in the case of the bisulphide being $4AgF + CS_2 = CF_4 + 2Ag_2S$ (Gore, *Proc. Roy. Soc.*, 1871, xx. 70).

(475) **FLUORIDE OF SULPHUR.**—Argentic fluoride is readily attacked by sulphur at a high temperature, argentic sulphide and fluoride of sulphur being produced. It is a colourless gas which does not condense at 0° (32° F.). It corrodes glass, fumes strongly in the air, and has a characteristic odour not unlike that of a mixture of chloride of sulphur and sulphurous anhydride (Gore, *loc. cit.*).

(476) **Determination of the Combining Proportion of Fluorine.**—Although the chemist has hitherto been unable to isolate fluorine in a state of purity, yet its combining proportion has been determined with precision; and the mode of proceeding offers an instructive illustration of the resources of chemical analysis in such a case.

The method of operating is as follows:—Pure fluor-spar is reduced to an impalpable powder, and dried; 10 grams of this powder are accurately weighed

into a counterpoised platinum crucible, and concentrated sulphuric acid, also perfectly pure, is added in quantity sufficient to reduce the whole to the consistence of cream: after standing for some hours, the excess of acid is expelled by the heat of a lamp: the temperature is raised very cautiously, and the crucible and its contents are finally heated to bright redness. In this operation the whole of the fluorine unites with the hydrogen of the sulphuric acid, and is expelled in the form of hydrofluoric acid, whilst the calcium takes the place of the hydrogen in the sulphuric acid, and forms calcic sulphate, which remains behind. On weighing the crucible after the experiment is completed, the calcic sulphate will be found to amount to 17·436 grams.

Now it is known that 136 parts of calcic sulphate, $CaSO_4$, contain 40 of calcium:

$$\text{but } 136 : 40 :: 17{\cdot}436 : x (= 5{\cdot}128);$$

17·436 grams of calcic sulphate must consequently contain 5·128 of calcium; 100 parts, therefore, of fluor-spar, if it consist only of fluorine and calcium, must be composed of 51·28 of calcium and 48·72 of fluorine. But although the atomic weight of the dyad metal calcium is 40, the quantity equivalent to the monad hydrogen is half that, or 20, so that the combining proportion of fluorine is found directly by the following calculation:

Qty. of calcium in 100 parts.		Equiv. of calcium.		Qty. of fluorine in 100 parts.		Equiv. of fluorine.
51·28	:	20	::	48·72	:	19.

The quantity of fluorine equivalent to 1 atom of hydrogen is thus ascertained to be 19.

CHAPTER XIII.

SILICON, OR SILICIUM: Si=28: *Tetrad, as in* $SiCl_4$.

(477) **SILICON** presents a certain analogy with boron in its tendency to unite with fluorine and with nitrogen. Silicon likewise exhibits a similar resemblance to titanium and tin in its power of forming an oxide with 2 atoms of oxygen, and in its production of a volatile liquid tetrachloride. The double fluorides which these elements form with the same bodies are isomorphous (*e.g.*, $SrF_2.SiF_4.2OH_2$; $SrF_2.SnF_4.2OH_2$; $SrF_2.TiF_4.2OH_2$). Zirconium forms a solid tetrachloride, but in properties it is nearly allied to silicon. The tetrad character of silicon, the existence of a hydride, SiH_4, analogous to marsh gas, CH_4, and the numerous compounds which may be obtained, possessing striking similarities in composition and constitution to organic substances, indicate that silicon is very nearly allied to carbon. These elements might be arranged thus in series:

Carbon	Tin
Silicon	Zirconium.
Titanium	

These elements all belong to the class of tetrads, being equivalent in their most usual combinations to 4 atoms of hydrogen.

Silicon when in combination with oxygen is the most abundant solid component of the earth's crust. It is the essential constituent of *Silex* or flint, hence the origin of the term silicon. In order to obtain the element in its uncombined form, a mixture of fluor-spar with fine quartzose sand or ground flints is heated with concentrated sulphuric acid; a gaseous tetrafluoride of silicon (480) is formed, which is partially soluble in water, producing an acid solution. The acid liquid, when neutralized with a solution of potassic hydrate yields a sparingly soluble salt, $2KF.SiF_4$. This potassic silicofluoride is to be thoroughly dried, and mixed in a glass or iron tube with eight- or nine-tenths of its weight of potassium, and heated. Potassic fluoride is formed, whilst silicon is reduced and partially combines with the excess of potassium; $2KF.SiF_4 + 2K_2 = Si + 6KF$. The mass, when cold, is treated with water, which produces a copious evolution of hydrogen, arising from the decomposition of the water by the excess of potassium. The washing with cold water is continued until it ceases to give any alkaline reaction with test-paper, and it is then finally well washed with boiling water, as long as anything is dissolved. Sodium may be advantageously substituted for potassium in this experiment, in the proportion of 1 part of sodium to 2 of the silicofluoride. Silicon may also be prepared by heating potassium or sodium in porcelain trays, in a glass tube, which is protected by lining it with thin plates of mica and passing a current of the vapour of silicic chloride over it.

Silicon may be obtained in two distinct modifications, viz., the *amorphous* and the *crystalline* modification.

1. Amorphous Silicon.—When procured by the processes above described, silicon presents the appearance of a dull brown powder, insoluble in water, in which it sinks. It is a non-conductor of electricity and soils the fingers when touched. Silicon is not acted upon by nitric or sulphuric acid, but is readily soluble in hydrofluoric acid, and in a warm solution of potassic hydrate. When heated in the air or in oxygen it burns brilliantly, and is converted into silica, which fuses from the intense heat, and forms a superficial coating over the unburnt silicon.

2. Crystalline Silicon.—The brown powder just described, if heated intensely in a closed platinum crucible, parts with a trace of hydrogen, shrinks greatly, becomes much denser, and darker in colour, and undergoes a remarkable change in properties.

After such ignition, the silicon may be heated strongly in air or in oxygen, even when urged in the blowpipe flame, without taking fire: it has become sufficiently heavy to sink in oil of vitriol, and resists the action of pure hydrofluoric acid, although it is rapidly dissolved if treated with a mixture of nitric and hydrofluoric acids. It may even be fused with nitre or with potassic chlorate without undergoing oxidation; but if the heat be urged to whiteness, the silicon burns brilliantly in the nitre: the oxidation, however, is much hastened by the addition of a little potassic carbonate, the mixture then deflagrates briskly, even when the temperature is much lower: by fusing with potassic carbonate alone, silicon is easily and completely oxidized; in both cases silica is formed, and is dissolved by the melted alkaline carbonate, displacing a portion of its carbonic anhydride. The properties of this compact form of silicon much resemble the *graphitoid* modification described by Deville and by Wöhler, who obtained the silicon in crystalline plates, by treating an alloy of silicon and aluminium in succession with boiling hydrochloric and hydrofluoric acids,* when the silicon remains behind in the form of plates,† which have a density of 2·49, and a metallic lustre. It may also be obtained by fusing 1 part of aluminium with 5 of glass free from lead, and 10 of powdered cryolite, treating the black mass with hydrochloric acid, and then with hydrofluoric acid. In this form silicon is a conductor of electricity; it may be heated to whiteness in a current of oxygen without undergoing change, but it is gradually dissolved by a mixture of hydrofluoric and nitric acids, although it is oxidized but very slowly when fused with potassic hydrate. When heated in a current of hydrochloric acid, a volatile liquid, silicon chloroform or silicic hydrotrichloride, $SiHCl_3$, is formed (486), whilst hydrogen gas is liberated.

According to Deville (*Ann. Chim. Phys.*, 1857, [3], xlix. 65), silicon requires for its fusion a temperature between the melting-point of cast iron and that of steel. In order to fuse it, he introduces the silicon into a platinum crucible lined with lime and

* Silicon appears to have the same sort of tendency to combine with aluminium that carbon has to unite with iron. The alloy is easily formed by heating aluminium in a Hessian crucible with from 20 to 40 times its weight of dry potassic silicofluoride, fusing the two together for a quarter of an hour, and then allowing the crucible to cool slowly.

† Prof. W. H. Miller has shown (*Proc. Roy. Soc.*, 1866, xv. 11) that the plates of so-called *graphitoid* silicon are really only modifications of the octohedral form, in which two parallel faces are much larger than any of the other faces, whilst two other parallel faces are either too small to be observed, or are altogether wanting.

protected by an outer clay crucible: the whole is then intensely heated in a wind furnace. If the lining of lime cracks, and the silicon reaches the platinum, the crucible is spoiled, owing to the formation of a platinum silicide. Fused silicon may also be procured when the mixture of sodic chloride with reduced silicon (obtained by igniting sodium in the vapour of silicic chloride), detached as far as possible from adhering fragments of porcelain, is placed in a crucible lined with charcoal, and exposed to intense heat in a forge; the sodic chloride becomes volatilized, and the silicon is fused into globules in the midst of the melted mass. These globules frequently show well-marked indications of crystallization: they have a dark, steel-grey colour, and a lustre like that of specular iron ore: now and then the silicon is found crystallized in regular double six-sided pyramids. It may also be obtained in regular six-sided prisms, terminated by three-sided pyramids, derived from the octohedron, by exposing pure aluminium in porcelain trays, heated intensely in a porcelain tube, to a current of the vapour of silicic chloride: the aluminium is volatilized as aluminic chloride, leaving the silicon in crystals which have a reddish lustre; they are hard enough even to cut glass like the diamond. Crystals of silicon may likewise be procured, and with less difficulty, by heating an earthen crucible to redness, and introducing a mixture of 3 parts of potassic silicofluoride with 1 part of sodium, cut into small pieces, and 4 of pure granulated zinc. The mixture must be maintained at a red heat, but below the temperature necessary to volatilize the zinc, until the slag is completely melted: it must then be allowed to cool slowly. The mass of zinc thus obtained contains long needles of silicon formed of octohedra, inserted one into the other: much of the zinc may be extracted by partial fusion at a low temperature, and the zinc which runs from the pasty mass in which the silicon is retained may be employed again in a similar operation: the zinc which still adheres to the silicon may be removed by digestion, first in hydrochloric, and afterwards in boiling nitric acid. If a very high temperature be employed in this operation the whole of the zinc may be expelled, and the silicon obtained in the fused condition. Deville and Caron have in this way (*Ann. Chim. Phys.*, 1863, [3], lxvii. 440) fused several hundred grams of silicon under a layer of potassic silicofluoride at a temperature near that at which cast iron melts, and have cast it into large cylindrical bars without sensible loss by oxidation. These bars exhibited a brilliant surface, which was not altered by exposure to the air.

Silicon forms but a single oxide, the well-known compound, silica, or silicic anhydride.

Wöhler has, however, discovered a remarkable series of compounds into the composition of which both oxygen and hydrogen enter: one of these he calls *silicon* ($Si_6H_6O_4$?) reserving the term silicium for the element; another he has named *leukon*, $Si_3H_4O_5$? (494); these bodies are possibly analogous to those obtained by Brodie from graphite (*note*, p. 101).

(478) **SILICIC HYDRIDE**; SiH_4.—Wöhler and Buff have described a remarkable gaseous combination of hydrogen and silicon. It may be obtained mixed with a large quantity of free hydrogen as a spontaneously inflammable gas, when a wire or plate of aluminium combined with silicon is placed in a solution of sodic chloride and made the positive pole of a feeble voltaic battery. A large surface of aluminium and the avoidance of any considerable elevation of temperature are necessary to insure the maximum production of the hydride.

Hydride of silicon may also be obtained by decomposing impure silicide of magnesium with cold dilute hydrochloric acid; the silicide is obtained by mixing intimately 40 parts of fused magnesic chloride, 35 of dried sodic silicofluoride, and 10 of fused sodic chloride; these are mixed in a warm dry tube, with 20 parts of sodium in small fragments, and thrown into a red-hot Hessian crucible, which is immediately covered; the heating is to be continued until the vapours of sodium cease to burn. It is also formed by the action of sodium on triethylic silico-formate, $SiH(OC_2H_5)_3$.

The electrolytic gas is colourless: when allowed to burn in the air, it emits white fumes, consisting of amorphous silica. If a cold plate of porcelain or of glass be introduced into a jet of the burning gas, a brown film of silicon is deposited upon its surface. It is also decomposed when passed through a glass tube heated to redness, a coating of silicon being deposited, and the gas is found to have lost its self-lighting power. This gas precipitates many metallic solutions, such as cupric sulphate, argentic nitrate, and palladious chloride, but is without action upon solutions of lead and of platinum; the precipitates in most cases contain silicon.

Pure silicic hydride has been obtained by the decomposition of an organic silicon compound called triethylic silicoformiate in contact with sodium. In this state it is not spontaneously inflammable at the ordinary temperature, but becomes so when diluted with hydrogen, or if gently heated, or when mixed with

air under reduced pressure (Friedel and Ladenburg, *Bull. Soc. Chim.*, 1867, [2], vii. 322).

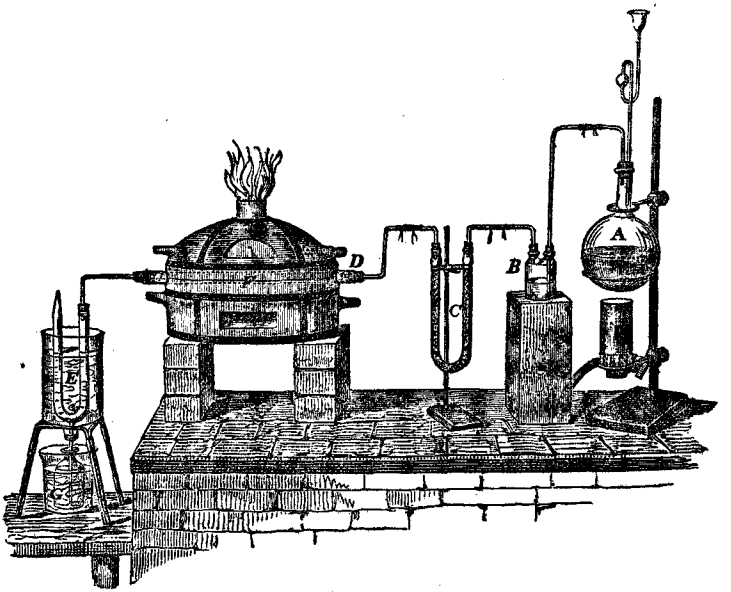
(479) **CHLORIDES OF SILICON.**—Three compounds of silicon are known, the tetrachloride, sesquichloride, and dichloride, although but little is known about the latter at present:

Silicic tetrachloride	...	...	$SiCl_4$ = 170
Silicic sesquichloride	...	...	Si_2Cl_6 = 269
Silicic dichloride	...	...	Si_2Cl_4 = 198

These compounds are analogous to the corresponding carbon compounds, carbonic tetrachloride or tetrachlormethane, CCl_4, perchlorethane, C_2Cl_6, and perchlorethylene, C_2Cl_4.

(480) **SILICIC TETRACHLORIDE**; *Chloride of Silicon:* $SiCl_4$=170; *Mol. Vol.* [ ]; *Rel. wt.* 85; *Theoretic Density of Vapour*, 5·882; *Observed*, 5·939; *of Liquid*, 1·5241 at 0° (32° F.); *Boiling-pt.* 57°·6 (135°·7 F.).—This compound may be formed by heating silicon in chlorine; but in practice it is obtained by the following indirect method:—Finely powdered silica is made up into a paste with oil and charcoal, and heated in a covered crucible; the charred mass in fragments is transferred to a porcelain tube, in which it is ignited, and subjected to a current of dry chlorine: neither chlorine nor carbon separately can decom-

FIG. 327.



pose silica, but together they effect its decomposition easily, carbonic oxide escaping, whilst silicic chloride is formed;

$SiO_2 + 2Cl_2 + C_2 = 2CO + SiCl_4$. The product is received into vessels cooled with a freezing mixture.

Fig. 327 shows a form of apparatus by which the chloride may be readily prepared: D is a porcelain tube, which contains the mixture of charcoal and silica; chlorine is liberated from the flask A, washed with water in B, dried by pumice and sulphuric acid contained in the tube C, and then passed through the tube D, which with its contents is exposed to a red heat in the furnace; silicic chloride distils over into the bent tube, E, where it is condensed by a freezing mixture of ice and salt; a tube fused into the bend of the tube E, conveys the chloride into a bottle, G, which may also be kept cool by ice.

Silicic chloride after the free chlorine has been removed by agitation with mercury and it has been redistilled, is a transparent, colourless liquid, with a pungent, acid, irritating odour; it is very volatile, and fumes strongly in the air. Its composition is the following:

		By weight.		By vol.
Chlorine	Cl_4 = 142	or 83·53	...	4
Silicon	Si = 28	16·47	...	1
Silicic chloride	$SiCl_4$ = 170	100.00	...	2

Water immediately decomposes silicic chloride, depositing hydrated silica, and forming hydrochloric acid. A moist atmosphere also decomposes the chloride, causing the deposition of silica in opaque lamellar plates, which like the mineral *hydrophane* become transparent when immersed in water, but resume their opacity on drying: the siliceous deposit obtained from the joints of the bamboo, and known as *tabasheer*, exhibits the same peculiarity. The liquid chloride does not act on potassium, but if the metal be heated in its vapour, potassic chloride is produced, and silicon is set free; this is one of the best methods of obtaining silicon.

(481) **SILICIC SESQUICHLORIDE**; *Silicon trichloride*, $Si_2Cl_6 = 269$.—When silicic tetrachloride is passed over silicon heated nearly to the softening point of porcelain, it is to a small extent converted into lower chlorides of silicon. As these, however, readily become dissociated, it is necessary to employ a central cooling tube (as in Deville's experiments on dissociation) through which water at 60° (140° F.) is passed. The apparatus is so arranged that the condensed vapours, consisting of the tetrachloride with a small proportion of lower chlorides, run back into the vessel containing the boiling tetrachloride, whence the tetrachloride (as it boils at a much lower temperature than the other products) again passes through the apparatus. The product contains, besides the sesquichloride, some unchanged tetrachloride and some oxychloride, since it is very difficult entirely to exclude the air during the operations. The sesquichloride can be obtained in the pure state only by repeated fractional distillation, for although the tetrachloride is easily separated, this is not the case with the oxychlorides. The sesquioxide is also formed along with the tetrachloride on distilling the sesquiiodide with mercuric chloride.

Pure silicic sesquichloride, Si_2Cl_6, which is analogous in composition to

carbonic sesquichloride (perchlorethane), C_2Cl_6, is a colourless, very mobile liquid of density 1·58 at 0° (32° F.). It solidifies at −1° (30°·2 F.), and boils at 146°—148° (294°·8—298°·4 F.). When its vapour is strongly heated in air it burns. In a closed vessel it begins to decompose at 350° (662° F.), and at 800° (1472° F.) is almost entirely resolved into silicon and silicic tetrachloride. The sesquichloride is decomposed by ammonia solution with formation of silica and evolution of hydrogen, whilst with water at 0° (32° F.) it yields a hydrated sesquioxide, $Si_2O_3.OH_2$ (492) (Friedel, *Compt. Rend.*, 1871, lxxiii. 1011; Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [5], vii. 476).

(482) **SILICIC DICHLORIDE,** ? $Si_2Cl_4 = 198$, is a liquid which is formed along with the sesquichloride, when a very high temperature is employed, and especially when the sesquichloride is accompanied by the highly condensed oxychlorides: it has not, however, yet been obtained free from oxychlorides. Like the sesquichloride, its vapour takes fire in air below a red heat, and it is decomposed by ammonia solution, but the proportion of hydrogen given off is larger. With water it yields an oxide different from that obtained from the sesquichloride.

(483) **SILICIC OXYCHLORIDES.**—Numerous compounds containing silicon, oxygen, and chlorine are known, many of which are formed by the action of the electric spark on a mixture of oxygen with the vapour of silicic tetrachloride or by passing them through a red-hot tube: they are consequently always found accompanying the sesquichloride, since it is very difficult completely to exclude oxygen during its preparation. The formulæ of those oxychlorides which have been isolated are as follows:

Empirical formula.	Formula corresponding to 2 vapour vols.	Boiling point °C.
Si_2OCl_7	—	—
Si_2OCl_6	Si_2OCl_6	136—139
$Si_4O_3Cl_{10}$	$Si_4O_3Cl_{10}$	152—154
$Si_2O_2Cl_4$	$Si_4O_4Cl_8$	198—202
$Si_4O_5Cl_6$	$Si_8O_{10}Cl_{12}$	about 300
$Si_4O_6Cl_2$	—	above 400
Si_4O_7Cl	—	—

The oxychloride, Si_2OCl_6 may be prepared by the action of silicic tetrachloride vapour on felspar at a very high temperature, the oxygen being derived from the latter, the more volatile portions of the distillate being repeatedly passed over the felspar. The oxychloride may be separated from the product by fractional distillation. It is also formed by the action of silicic tetrachloride on phosphoric anhydride at a high temperature. This oxychloride is a colourless fuming liquid which boils at 136°—139° (276°·8—282°·2 F.); in contact with water it is decomposed, yielding silica and hydrochloric acid. The other oxychlorides are most readily obtained by passing a mixture of oxygen with the oxychloride, Si_2OCl_6, through a red-hot tube: they are all liquids with exception of the compound, $Si_4O_7Cl_2$.

(484) **SILICIC TETRABROMIDE;** $SiBr_4$; *Density of Liquid* at 0° (32° F.) 2·813; *Boiling-pt.* 153° (307°·4 F.), is analogous in properties to the chloride; it may be formed in a similar manner.

Silicic Sesquibromide, Si_2Br_6, is prepared by adding an equivalent quantity of bromine to silicic sesquiiodide dissolved in carbonic bisulphide. The precipitated iodine is removed by filtration, and what remains dissolved in the carbonic bisulphide, by agitation with mercury. On evaporation, crystals of the sesquibromide are obtained, which fuse when heated, and distil at about 240°

(464° F.) without decomposition. The crystals are doubly refractive (Friedel, *Compt. Rend.*, 1871, lxxiii. 1011).

(485) **SILICIC IODIDES.**—Two iodides are known, the *tetriodide*, SiI_4, a substance crystallizing in colourless transparent octohedrons, which melt at 120°·5 (248°·9 F.) to a yellowish liquid, boiling at about 200° (392° F.), and which may be distilled in a current of carbonic anhydride without alteration. It is formed by passing iodine vapour mixed with carbonic anhydride over silicon heated to redness, when it condenses in the cool part of the tube as a colourless crystalline mass. If excess of iodine has been employed, the sublimed iodide is mixed with the latter, but may be readily obtained pure by dissolving it in carbonic bisulphide—in which it is readily soluble—and agitating the solution with mercury to remove the iodine.

Silicic Sesquiiodide, Si_2I_6, is formed on digesting the tetriodide with finely divided silver nearly at its boiling point; the colourless mass thus obtained may be freed from unaltered tetriodide by washing with successive small quantities of carbonic bisulphide, and finally purified by crystallization from that solvent, in which it is much less soluble than the tetriodide. It crystallizes in beautiful colourless hexagonal prisms or rhombohedra, which melt at 256° (482° F.), but at the same time partially decompose. It cannot be distilled, as when strongly heated it splits up into the tetriodide, and a *subiodide* of an orange-red colour, which appears to be the diiodide, Si_2I_4. The sesquiiodide is decomposed by water in the same way as the sesquichloride, yielding the compound $Si_2H_2O_4$ (Friedel, *Ann. Chem. Pharm.*, 1869, cxlix. 96; and *Compt. Rend.*, 1871, lxxiii. 497).

(486) **SILICIC CHLOROFORM;** $SiHCl_3$; *Density of Vapour*, 4·64; *Boiling-pt.* 35°—37° (95°—98°·6 F.).—This body mixed with silicic chloride constitutes the hydrochlorate of chloride of silicon or chloroleukon ($Si_3H_4Cl_{10}$ = $4HCl.3SiCl_2$) of Wöhler and Buff (*Ann. Chem. Pharm.*, 1857, civ. 94). It is obtained by passing hydrochloric acid over heated crystallized silicon and condensing the product in a tube surrounded by a freezing mixture; by fractional distillation, the silicon chloroform is separated from the silicic chloride.* It is a colourless, highly mobile liquid, which fumes powerfully on exposure to the air, depositing a white film upon surrounding bodies, and emitting a vapour of suffocating odour. It is highly inflammable, and burns with a greenish, feebly luminous flame, depositing silica and emitting hydrochloric acid. If its vapour be mixed with oxygen, it explodes violently on passing the electric spark, silica being deposited, whilst hydrochloric acid and silicic chloride are formed. The liquid may be boiled with sodium without undergoing decomposition. If passed through a tube heated to redness, it is decomposed into a mixture of silicic chloride and hydrochloric acid, whilst half its silicon is deposited in the form of a brown amorphous crust exhibiting a metallic lustre. Water decomposes it immediately with great elevation of temperature, leukon and hydrochloric acid being formed: $2SiHCl_3 + 3OH_2 = 6HCl + Si_2H_2O_3$.

When hydriodic acid mixed with hydrogen is passed over heated silicon, a mixture of solid silicic iodide with liquid *silicic iodoform*, $SiHI_3$, is produced. This is a colourless, strongly refracting liquid of density 3·362 at 0° (32° F.) and boiling at 220° (428° F.).

(487) **FLUORIDE OF SILICON;** *Silicic tetrafluoride*, $SiF_4 = 104$; *Rel. wt.* 52; *Theoretic Density*, 3·598; *Observed*, 3·60; *Mol. Vol.* [ ].—This fluoride is one of the most remark-

* A corresponding bromine compound, *silicic bromoform*, is also obtained in passing hydrobromic acid over heated silicon. It is a colourless liquid.

able compounds of silicon: so powerful is the attraction between fluorine and silicon that hydrofluoric acid separates silicon from its most intimate combinations, such as silica and glass. In order to prepare silicic fluoride, equal parts of finely powdered fluor-spar and siliceous sand, or powdered glass, are mixed in a capacious flask or retort, with twelve times their weight of oil of vitriol. On the application of heat, a colourless gas, with a peculiar, pungent, suffocating odour is given off; hydrofluoric acid is liberated, and this immediately attacks the silica, as is shown in the following equations:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4;$$
$$\text{and } 4HF + SiO_2 = 2OH_2 + SiF_4.$$

The composition of the gas may be thus represented:

			By weight.		By vol.
Silicon	Si	= 28	or 26·9	...	1
Fluorine... ...	F_4	= 76	73·1	...	4
Silicic Fluoride ...	SiF_4	= 104	100·00	...	2

Silicic tetrafluoride fumes strongly in the air; it is not inflammable, but extinguishes a lighted taper; under strong pressure it was liquefied by Faraday; and according to Natterer it becomes solid at $-140°$ ($-220°$ F.). The gas is dissolved and partially decomposed by water; it must therefore be collected over mercury, and in jars which have been perfectly dried at a high temperature; the slightest trace of moisture on the surface of the jar causes a deposition of silica, which adheres very firmly to the glass, and renders it opalescent. Silicic fluoride combines with twice its volume of ammoniacal gas, and forms with it a volatile crystalline compound.

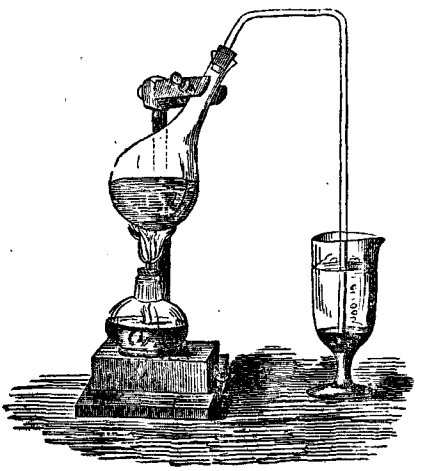
A subfluoride, probably the *sesquifluoride of silicon*, Si_2F_6, is formed when a rapid current of silicon tetrafluoride is passed over silicon at a temperature approaching that at which porcelain softens. It is a light white volatile powder, which is decomposed at a red heat into silicon and the tetrafluoride; it behaves with reagents in a manner similar to the sesquichloride, and like it yields a hydrated suboxide by the action of water (Troost and Hautefeuille, *Ann. Chim. Phys.*, 1876, [5], vii. 453).

(488) **SILICOFLUORIC ACID**; *Hydrofluosilicic Acid*, $H_2F_2.SiF_4$ or $H_2SiF_6 = 144$.—When a stream of gaseous silicic fluoride is passed into water, it is decomposed and partially dissolved. Two molecules of water react on 3 of the fluoride, and produce silicofluoric acid which is dissolved, whilst one-third of its silicon is deposited as silica in a hydrated form:

$$3SiF_4 + 2OH_2 = SiO_2 + 2(H_2F_2.SiF_4).$$

In the preparation of this acid, the end of the tube from which the fluoride is escaping must not come in contact with the water, otherwise it will speedily become obstructed by the deposited silica. This may be obviated by placing a little mercury at the bottom of the vessel, in order that the orifice of the tube may dip beneath the mercury, as shown in fig. 328. Each bubble as it rises is surrounded by a siliceous envelope, so that the liquid finally becomes a gelatinous mass; this is submitted to pressure in a linen cloth, by which means the solution of silicofluoric acid is separated from the deposit of silica: the latter when thoroughly washed to free it from adhering acid, constitutes a pure hydrate of silica. A more easy method of obtaining the acid, when it is required in quantity, consists in dissolving silica in dilute hydrofluoric acid.

FIG. 328.



A saturated solution of silicofluoric acid forms a very sour, fuming liquid. In solution it does not attack glass, but it does so if allowed to evaporate upon it; silicic fluoride becomes volatilized, leaving free hydrofluoric acid, which, reacting on the silica of the glass, produces water and silicic fluoride, as in the ordinary process for making that gas; $4HF + SiO_2 = 2OH_2 + SiF_4$.

Silicofluoric acid combines with bases to form salts, but if an excess of base be employed, silica is precipitated, and the whole of the fluorine is separated as a metallic fluoride. In the first case the action may be thus represented:

$$2KHO + H_2SiF_6 = 2OH_2 + K_2SiF_6.$$

In the second case: $6KHO + H_2SiF_6 = 4OH_2 + 6KF + SiO_2$. A dilute solution of silicofluoric acid produces transparent jelly-like precipitates in the salts of the alkali-metals; it is frequently employed as a precipitant of potassium. With salts of barium the acid gives a white crystalline precipitate.

(489) **SILICIC ANHYDRIDE**, or *Silica*; *Silicic dioxide* ($SiO_2 = 60$); *Density Cryst.* 2·5—2·8; *Amorphous*, 2·2—2·3; *Comp. in* 100 *parts*, Si, 46·67; O, 53·33.—Berzelius represented this

compound as a trioxide, giving the atomic weight of silicon as 22, if that of oxygen be 8. There are, however, reasons which render it almost certain that it contains only 2 atoms of oxygen, and that it corresponds in composition to carbonic anhydride: for example, 1 molecule of silicic chloride, when converted into vapour, instead of forming an exception to the general rule, as it does upon the theory of Berzelius, would then produce 2 volumes of vapour as usual: and in decomposing fused potassic carbonate by the addition of finely divided silica, it is found that the whole of the carbonic anhydride is expelled when the proportion of silica is to the carbonate as 60 to 138.* According to the experiments of Dumas, 100 parts of silica contain 46·7 of silicon, and 53·3 of oxygen.

Silica occurs in two modifications, the crystalline and the amorphous. In the crystalline state it has the higher specific gravity.

Pure crystalline silica occurs in *rock crystal* and in some forms of *quartz*, crystallized in six-sided prisms, transversely striated, and terminated by six-sided pyramids. *Amethyst* is a purple variety coloured with an oxide of iron (ferric acid?). Silica is found nearly pure in *agate* and *calcedony*, which consist of a mixture of the crystallized and amorphous varieties. Calcedony in alternate layers of different colours constitutes *onyx*. *Carnelian* is a red or brown variety containing ferric oxide. *Flint* is a variety of calcedony, chiefly found in the upper chalk; and *opal* consists of the amorphous variety of silica with a varying quantity of water. Silica constitutes the principal ingredient of all sandstones, and it enters largely into the composition of felspar, and of a vast variety of minerals. Pure crystallized silica is perfectly transparent and colourless; in hardness it approaches the precious gems. It fuses in the flame of the oxyhydrogen blowpipe to a transparent glass, which may be drawn out into fine, flexible, elastic threads of the amorphous variety. Native silica is insoluble in water, and in all acids except hydrofluoric.

Preparation.—Finely divided silica has the aspect of a white earth, and although insoluble, it possesses the power of uniting

* The experiments of Colonel Yorke (*Phil. Trans.*, 1857) have, however, shown that the proportion of carbonic anhydride expelled by equal weights of silica from an excess of the different carbonates, varies with the nature of the base; sodic carbonate losing a larger proportion than potassic carbonate, and lithic carbonate more than sodic carbonate, when equal quantities of silica were employed.

with bases, as is shown by the usual process for obtaining it in a state of purity:—A mixture of potassic and sodic carbonates is fused at a red heat, and one-third of its weight of ground flint, or some other siliceous mineral in fine powder, is added in small quantities at a time to the melted mass; on each addition a brisk effervescence, due to the escape of carbonic anhydride, takes place. When all the mineral has been introduced, the mixture is heated strongly for some minutes, and is then allowed to cool; on being digested with water, the mass slowly dissolves with the exception of a portion of the impurities, such as ferric oxide and titanic anhydride, which the siliceous material may have contained. A larger quantity of silica than that above indicated would still yield a mixture which might be fused by a strong heat; but it becomes less soluble in proportion to the excess of silica, until at length a point is reached at which it is no longer soluble in water or in the common acids; indeed, it forms the basis of glass. When it is proposed to obtain pure silica, therefore, an excess of alkali is always used, as the resulting compound is then easily attacked by acids, in which it is entirely soluble if the acid be dilute and in sufficient quantity. If the solution in hydrochloric acid be evaporated, the silica is separated as a gelatinous hydrate, which, by continuing the heat, is converted into a white earthy-looking powder no longer soluble in acids: after being digested with oil of vitriol to remove traces of titanic anhydride, and decanting the strong acid, it is well washed as long as anything is dissolved; if then dried and ignited, it is perfectly pure. As thus prepared, silica, like charcoal and other porous bodies, absorbs aqueous vapour rapidly from the air, without becoming sensibly moist.

Perfectly pure silica may also be procured by passing gaseous silicic fluoride into water; a decomposition of the gas occurs, and one-third of the silicon it contains is deposited as silica in white hydrated flocks, which, if washed and ignited, furnish silica of snowy whiteness; $3SiF_4 + 2OH_2$, yielding $SiO_2 + 2H_2SiF_6$. Silica may likewise be obtained nearly pure by heating colourless quartz to redness, and quenching it in water; the mineral is rendered friable by this treatment, and is then easily reduced to a fine powder: common flints treated in a similar manner give a very white powder, which is nearly pure silica. All the artificial forms of silica are amorphous, and are much more easily attacked by solvents than the crystalline variety.

(490) **Hydrates of Silica.**—Insoluble, however, as silica generally is in water, and although silica, when once deposited,

even in the gelatinous form, is almost insoluble both in water and in acids, a modification of it exists which dissolves completely at the moment of its liberation from some of its compounds which are already in solution. For instance, if a dilute solution of an alkaline silicate be poured into a considerable excess of hydrochloric acid, the whole of the silica is retained in solution; but it may be precipitated from this acid solution by the gradual addition of a solution of potassic hydrate, so as to neutralize the acid; and if hydrochloric acid be gradually added to a solution of an alkaline silicate in water, the silica is precipitated in a gelatinous form in proportion as the alkali is neutralized.

From the solution of alkaline silicate in excess of hydrochloric acid, Graham obtained a pure solution of hydrated silica, by subjecting the liquid to dialysis in a hoop dialyser of parchment-paper (62). If a stratum of liquid 4 tenths of an inch (1 centimetre) in depth be subjected for 4 or 5 days to dialysis, changing the water in the outer vessel at intervals of 24 hours, the hydrochloric acid and the soluble chlorides will be found to have diffused so completely that the liquid in the dialyser will give no precipitate with argentic nitrate.

A solution prepared in this way and containing 5 per cent. of silica may be concentrated until the quantity of silica reaches 14 per cent. if the liquid be boiled down in a flask. In open vessels it is apt to gelatinize on the edge, and the whole then solidifies. The solution is tasteless, limpid, and colourless, with a feebly acid reaction, rather greater than that of carbonic acid; 100 parts of silica require 1·85 of potassic oxide, K_2O, to neutralize this effect on litmus. The solution is not easily preserved for many days, as it becomes converted into a solid transparent jelly which, even in closed vessels, shrinks, whilst water is separated from it. The coagulation is retarded by hydrochloric acid, and by small quantities of potassic or sodic hydrate. Sulphuric, nitric, and acetic acids are without action on the solution, but it is slowly coagulated by a few bubbles of carbonic anhydride. Its coagulation is also effected in a few minutes by the addition of $\frac{1}{10,000}$ part of any alkaline or earthy carbonate in solution, but neither by caustic ammonia nor by neutral nor acid salts. Alcohol and sugar, gum and caramel, are without action, but solutions of gelatin, soluble alumina, and soluble ferric oxide, immediately cause a gelatinous precipitate; when a solution of silica is gradually added to one of gelatin in excess, the precipitate obtained consists of ·100 of silica and 92 of gelatin (*Phil. Trans.*, 1861, p. 204).

By evaporation *in vacuo* at 15° (59° F.), the silica is left behind in the form of a transparent glassy mass of great lustre, containing, after exposure for two days over sulphuric acid, 21·99 of water, which corresponds nearly to the formula, $OH_2.SiO_2$ or H_2SiO_3.*

There is, however, considerable difficulty in obtaining a definite hydrate of silica, for it easily loses a portion of its water at low temperatures, and is moreover a very hygroscopic substance. The following compounds have been obtained, however:

* $[SiO(OH)_2]$.

$3OH_2.2SiO_2$ $OH_2.3SiO_2$
$OH_2.SiO_2$ $OH_2.4SiO_2$
$4OH_2.9SiO_2$ $OH_2.8SiO_2$.
$OH_2.2SiO_2$

Ebelmen, by the action of moist air upon silicic ether, obtained a transparent, glassy hydrate, which had a composition represented by the formula $3OH_2.2SiO_2$;* and a compound which gave similar results on analysis was procured by Doveri, on drying the ordinary gelatinous hydrate of silica *in vacuo* over sulphuric acid without the aid of heat; whilst Merz (*Jour. pr. Chem.*, 1866, xcix. 177), on treating the hydrate prepared by passing silicic fluoride into water in a similar manner, found the compound to be $OH_2.3SiO_2$; dried in air at the ordinary temperature, its composition was $OH_2.2SiO_2$. Fuchs obtained two hydrates of silica, one containing from 9·1 to 9·6 per cent. of water, corresponding to the formula $OH_2.3SiO_2$,† which requires 9·1 per cent., the other between 6·6 and 7 per cent., agreeing nearly with the formula $OH_2.4SiO_2$,‡ which would contain 6·9 per cent. of water. From the occurrence of a mixed ether consisting of $C_5H_{11}.3C_2H_5.SiO_4$,§ it appears that the silicic is really a tetrabasic acid, although from the facility with which its basic hydrogen escapes as water, the composition of the hydrate is doubtful.

A very white and light hydrate of silica occurs naturally in abundance in beds situated at the base of the chalk formation, between the upper greensand and the gault; the proportion of hydrated silica in these deposits varies very greatly, ranging from 5 to as much as 72 per cent., being most abundant in the upper portion of the deposit (Way). A mixture of this material with slaked lime, when made into a paste with water, is in few weeks converted into a silicate of lime, and the change is accelerated by the presence of 2 or 3 per cent. of soda.

Insoluble silica may be gradually converted into the soluble variety by long digestion with solutions of the alkalies. Even flints in their unground condition may be dissolved in strong solutions of caustic alkali (density 1·16), if the solution be digested with them under pressure at a temperature of between 150° and 200° (302° and 392° F.). Silica also in all its forms is soluble in aqueous ammonia, according to Pribram.

* $\left[\begin{matrix}Si(OH)_3\\O\\Si(OH)_3\end{matrix}\right]$.

† $\left[\begin{matrix}SiO(OH)\\O\\SiO\\O\\SiO(OH)\end{matrix}\right]$.

‡ $\left[\begin{matrix}SiO(OH)\\O\\SiO\\O\\SiO\\O\\SiO(OH)\end{matrix}\right]$.

§ $[Si(OC_2H_5)_3(OC_5H_{11})]$.

Finely divided hydrate of silica is also dissolved by the alkaline carbonates: these carbonates are only partially decomposed by the silica which is dissolved. It appears to be owing to the solubility of silica in solutions of the carbonates that almost all spring and river waters contain silica in solution in minute quantity; on evaporation the silica is obtained in the insoluble form. When the action of the alkaline liquid is aided by that of a high temperature, as is the case with the Geysers or boiling springs of Iceland, and of the Yellowstone River in America, very large quantities of silica are dissolved, which, as the liquid cools, are deposited as "petrifactions" on surrounding objects exposed in the basin or in the stream.

Tripolite, abundant deposits of which are found in Algiers, France, Barbadoes, and elsewhere, consists almost entirely of organic siliceous skeletons; the silica, which is hydrated, is readily soluble in a dilute solution of potassic hydrate; it is largely used as a polishing powder.

Silica also exists in the soluble form in a class of minerals termed zeolites, which are hydrated siliceous compounds found in the cavities of the amygdaloid rocks. The zeolites, if finely powdered, and treated with hydrochloric acid, swell up to a transparent jelly; this gelatinous mass consists of hydrate of silica.

These observations on the various conditions under which silica may be rendered soluble derive their interest from the extensive formation of crystallized silica, so abundantly diffused over the surface of the earth, and the difficulty of crystallizing it by artificial means. The zeolites represent the hydrated silica in a crystalline form, and quartz and agate the crystallized silicic anhydride.

(491) **Silicates.**—The silicates are most abundant natural productions. All the forms of clay, felspar, mica, hornblende, and a large number of other common minerals, are compounds of this description.

Silica combines with bases in several different proportions; most of its compounds are found in the form of crystallized minerals, many of which are double silicates of very complex composition. It is highly probable that silicic, like phosphoric acid admits of modifications which differ in basic power. Odling (*Phil. Mag.*, Nov. 1859) proposes to call the silicates of the type M_4SiO_4, *orthosilicates*; those of the type M_2SiO_3, *metasilicates*, with an intermediate class formed by the combination of one atom of each of the two. The combinations with bases which

are of most usual occurrence belong to one or other of the following classes, the orthosilicates being regarded as the *normal* salts:

Orthosilicates	Dioptase	... $Cu''H_2SiO_4$	$[Si(O_2Cu)''(OH)_2]$
M'_4SiO_4 or	Olivine	... $(MgFe)''_2SiO_4$	
M''_2SiO_4	Forge cinder	... Fe''_2SiO_4	$[Si(O_2Fe)''_2]$
Metasilicates	Wollastonite	... $Ca''SiO_3$	$[SiO(O_2Ca)'']$
M'_2SiO_3 or	Picrosmine	... $2(Mg''SiO_3).OH_2$	$[_2SiO(O_2Mg)''.OH_2]$
$M''SiO_3$	Augite	... $(CaMg)''SiO_3$	
$\frac{4}{3}$ Silicates	Meerschaum	... $Mg''_2SiO_4.(H_2SiO_3)$	
$M'_4SiO_4.2SiO_2$	Silicate of calcium	$Ca''_2SiO_4.2SiO_2$	
Acid silicates $M'_2SiO_3.SiO_2$ or $M''SiO_3.SiO_2$	The composition of many of the ordinary varieties of glass may be approximatively represented by mixtures of different silicates which have this formula.		

In the above formulæ M′ stands for 1 atom of any metallic monad, such as potassium, and M″ for 1 atom of any metallic dyad, such as calcium.

In most cases, however, in the formulæ of the silicates the custom of representing them as compounds of the bases with the anhydride silica will be adhered to. Their diversified forms have not hitherto been satisfactorily classified.

Most of the silicates are fusible; their fusibility is increased by mixture with each other; those which contain readily fusible oxides melt at the lowest temperature, and in general the basic silicates fuse more readily than those which are normal in composition, or which contain excess of silica. All the silicates are insoluble in water, with the exception of those of the alkalies which contain a large proportion of base. The hydrated silicates, and those which contain the largest proportion of base, are those most easily decomposed by acids; whilst the anhydrous normal and acid silicates of the earths are not decomposed by any acid except hydrofluoric. The silicates may be detected by fusing them with sodic or potassic carbonate, and then heating the residue with acid, and evaporating to dryness; on treating the product with hot water, the silica remains undissolved in the form of a white powder, which when fused with sodic carbonate upon platinum foil before the blowpipe, yields a colourless bead of glass. The freedom of silica from bases may be ascertained by its being volatilized without residue when evaporated in a platinum vessel with excess of pure hydrofluoric acid. Pure silica is not attacked by fusion with microcosmic salt, but is left as a spongy mass in the clear bead; if any earth or base be present, the bead is generally more or less opalescent. Borax dissolves silica slowly, when fused with it, forming a clear colourless bead.

The acid character is so feebly marked in silica, that the ordinary vegetable acids, such as acetic, oxalic, and tartaric, precipitate silica from its combinations with the alkalies; and a current of gaseous carbonic anhydride, or even the gradual absorption of carbonic acid from the atmosphere, produces a similar result. At a high temperature, however, the action is reversed; for as silica is not volatilized to any perceptible extent by the heat of a furnace, it decomposes the carbonates and the salts of all the volatile acids when ignited with them; hence even the sulphates yield up their bases to the silica, whilst the sulphuric anhydride is expelled.

(492) **SILICON-OXALIC ACID,** $Si_2H_2O_4$.—Although no oxides of silicon lower than silicic oxide or silica are known, compounds containing hydrogen, oxygen, and silicon have been obtained which may be supposed to be the hydrates of such oxides, one of these, which may be regarded as a compound of silicic sesquioxide with water, $Si_2O_3.OH_2$, or preferably as a dibasic acid of the composition $Si_2H_2O_4$ or $Si_2O_2(OH)_2$ analogous to oxalic acid, $C_2O_2(OH)_2$, is formed on treating the silicic triiodide or trichloride with water at 0° (32° F.), hydriodic or hydrochloric acid being produced at the same time. The hydrate may be freed from hydrochloric acid by washing with water, or the solution may be evaporated *in vacuo*, and the residue heated at 100° (212° F.). In the pure state it is a colourless substance, which decomposes with incandescence when strongly heated, giving off hydrogen and leaving silica. It is also decomposed by a solution of potassic hydrate, with formation of potassic silicate and evolution of hydrogen. It reduces potassic permanganate rapidly in the cold, but chromic acid only slowly. At ordinary temperatures it does not act on auric chloride or selenious acid.

(493) **SILICONE.**—If coarsely-powdered calcic silicide be digested in fuming hydrochloric acid, in a vessel kept cool by immersion in water, an evolution of hydrogen takes place, and a new compound is gradually formed; to this Wöhler (*Ann. Chem. Pharm.*, 1863, cxxvii. 263) has given the name of *silicon*, which is objectionable, because it has been already appropriated to the element itself. The mixture is to be agitated frequently and kept for some time in a dark place until no more gas is given off: it is then to be diluted with 7 or 8 parts of water, and the insoluble material collected, washed, pressed between blotting-paper, and dried in the dark *in vacuo*, over sulphuric acid.

Silicone ($Si_6H_6O_4$?), or *chryseon*, as it might be fitly termed in allusion to its colour, is a bright orange-yellow mass, insoluble in water, alcohol, carbonic bisulphide, phosphorous chloride, or silicic chloride. When heated, it deepens in colour, and afterwards takes fire with slight explosion and the emission of sparks, leaving silica, which has a brown colour due to the presence of silicon. If heated without access of air, it evolves hydrogen, leaving a residue of silica and amorphous silicon in shining brown flakes. The decomposition begins even at 100° (212° F.). If heated with water in a sealed tube at 196° (384°·8 F.), it is speedily converted into white flakes of silica, whilst pure hydrogen is liberated.

In the dark it may be preserved without alteration, either in a moist or dry state, but if exposed to diffused daylight, it slowly becomes paler, with evolution of hydrogen. If exposed to the sun's rays under water, it immediately begins to evolve hydrogen, and a white residue of silicon formanhydride is left, which Wöhler termed leukon (494).

Silicone is not attacked either by chlorine or by fuming nitric or sulphuric acid, even when boiling; but hydrofluoric acid dissolves it completely. Its characteristic reaction is the rapid manner in which it is dissolved by solutions of the caustic alkalies, with rise of temperature and copious evolution of hydrogen. Ammonia, even in very dilute solutions, has a similar effect. The carbonates of the alkali-metals dissolve it more slowly. Silicone acts as a powerful reducing agent, especially in the presence of alkalies. Salts of copper, gold, silver, palladium, and osmium yield with it dark silicates of a suboxide.

(494) **SILICON FORMANHYDRIDE**; *Leukon*, $Si_2H_2O_3$ $\left[\begin{matrix}SiHO\\O\\SiHO\end{matrix}\right]$.

—This compound was first described as a hydrated oxide of silicon, but it was subsequently examined by Wöhler (*Ann. Chem. Pharm.*, 1863, cxxvii. 268), who changed its name to leukon, in allusion to its aspect (from λευκὸς, white), and assigned to it the formula, $Si_8H_4O_5$. Friedel and Ladenburg (*Bull. Soc. Chim.*, [2], vii. 322), have since shown that this body is the analogue of the unknown formic anhydride.

Leukon may be prepared by placing crystallized silicon in a wide glass tube connected with a U-tube cooled by a mixture of ice and salt, whilst the apparatus terminates in a bent tube dipping into ice-cold water; the silicon is to be raised to a barely visible red heat, and a current of dry hydrochloric acid gas passed over it; silicon chloroform, $SiHCl_3$, is formed and in part condensed in the U-tube, whilst the portion which passes on is immediately decomposed by the water into hydrochloric acid and leukon; $2SiHCl_3 + 3OH_2 = 6HCl + Si_2H_2O_3$. The voluminous white precipitate thus obtained is to be quickly pressed between folds of blotting-paper and dried *in vacuo* over sulphuric acid. According to Friedel and Ladenburg, the best process is to pass the vapour of pure silicic chloroform (486) slowly into ice-cold water through a tube with a funnel-shaped opening to prevent its being stopped up.

When silicic dichloride is treated with water at 0° (32° F.), it yields a substance which rapidly decomposes not only potassic permanganate, but also chromic acid, auric chloride and selenious acid. It is possibly identical with the compound just described.

Leukon undergoes oxidation, and evolves hydrogen, in contact with water, at temperatures above 0° (32° F.). Wöhler and Buff (*Ann. Chim. Phys.*, 1858 [3], lii. 276) describe this body as a snow-white powder when dry, sufficiently light to float upon water, although it sinks in ether. The caustic alkalies and their carbonates dissolve it rapidly with brisk effervescence, forming a silicate of the base, whilst hydrogen escapes; ammonia also decomposes it with slow evolution of hydrogen. The acids, with the exception of the hydrofluoric, do not act upon it. It may be heated in air to 300° (572° F.) without alteration; but at a somewhat higher temperature it takes fire, burning with scintillation, and emitting a phosphorescent light. If heated in a closed crucible it is decomposed into a mixture of silicon and silica, whilst silicic hydride (479) is liberated, but undergoes immediate decomposition. Leukon is slightly soluble in water, but the liquid rapidly decomposes with evolution of hydrogen gas. The solution exerts a strong reducing power, precipitating gold and palladium in a metallic form, from neutral solutions of their salts. It also throws down reduced selenium and tellurium from solutions of selenious and tellurous acids in hydrochloric acid, and instantly bleaches a solution of potassic permanganate. Wöhler and Buff, however, think it probable that this solution contains a still lower oxide of silicon than the one above described.

(495) **SILICIC NITRIDE**, or *Nitride of Silicon*, may be obtained by the direct action of nitrogen upon silicon at a very high temperature; crystallized silicon, when heated in nitrogen gas, becoming coated with a light, bluish, fibrous compound of the two elements. This nitride may be heated to redness in chlorine without undergoing decomposition. When heated to full redness in a current of steam, ammonia is disengaged abundantly and silica is formed.

(496) **SILICIC SULPHIDE**: $SiS_2 = 92$.—A bisulphide corresponding in composition to silica is formed on passing the vapour of carbonic bisulphide over a mixture of finely divided silica and carbon; or when compact or pulverulent silicon is strongly heated in an atmosphere of sulphur, the two elements combining with a red glow; a white earthy-looking bisulphide, which absorbs moisture rapidly from the air, is the result: this compound is completely soluble in water, but is at the same time decomposed, $SiS_2 + 2OH_2$ becoming $SiO_2 + 2SH_2$; sulphuretted hydrogen and soluble silica being formed: the silica may be obtained as a jelly by evaporation.

Two compounds of silicic sulphide and chloride have been obtained, having the formulæ $SiS_2.2SiCl_4$ (*Density of Vapour** 5·24), and $2SiS_2.SiCl_4$.

When a mixture of silicic tetrachloride and hydrogen sulphide is passed through a red-hot tube, a reaction takes place which may be represented by the following equation: $SiCl_4 + SH_2 = SiCl_3.HS + HCl$. The *silicic hydrosulphochloride*, $SiCl_3.HS$, thus obtained is a colourless liquid boiling at 96° (204°·8 F.). It is decomposed by water, yielding silicic acid, hydrochloric acid, and sulphuretted hydrogen. Its *Vapour density* is 7·25, *Theoretic* 7·42 (Pierre, *Ann. Chim. Phys.*, 1848, [3], xxiv. 268; Friedel and Ladenburg, *ibid.*, 1872, [4], xxvii. 416).

CHAPTER XIV.

PENTAD ELEMENTS.

(497) THE typical pentad element, nitrogen, has already been described: it will only be necessary in this place to consider phosphorus, the remaining members of the group, vanadium, arsenicum, antimony, bismuth, tantalum, and niobium, being placed amongst the metals. There is not the same great resemblance between the elements of this group as exists in the case of the halogens, the analogies being insignificant in some cases although strongly marked in others. The similarities between the corresponding compounds are much more striking than

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* The vapour density of this compound is anomalous, for the formula above given corresponds to 3 instead of 2 volumes of vapour, or 1 vol. of the vapour of silicic bisulphide and 2 of the tetrachloride united without condensation:

		By volume.
SiS_2	=	1
$2SiCl_4$	=	2
		3

between the elements themselves, which differ very widely from one another in character.

In a large number of their compounds these elements exist in the tervalent or triad condition representing three atoms of hydrogen: they are also sometimes quinquivalent or pentads. Phosphorus, arsenicum, and antimony form gaseous hydrides in which 3 volumes of hydrogen combine with $\frac{1}{2}$ a volume of the vapour of the other element—the compounds which are formed occupying the space of 2 volumes—these gaseous compounds exhibiting a tendency to alkalinity, and form derivatives much resembling those of ammonia. Each of these elements unites with oxygen in the proportion of 2 atoms to 3, and 2 to 5, forming compounds in which the acid character is less and less marked as the atomic weight of the combustible element increases. The isomorphous relations of arsenious anhydride and antimonious oxide have long been known, and the corresponding tribasic phosphates and arseniates also offer some of the most striking exemplifications of isomorphism. Chlorine unites with the members of this group in the proportion of 3 atoms to 1 atom of phosphorus, arsenicum, or antimony. Bismuth is also related to this group by the composition and character of its oxides and chloride; although no compound of bismuth and hydrogen is at present known. Nitrogen, as already pointed out, is connected with the phosphorus group by its combination with hydrogen, NH_3, and by its formation of anhydrides with 3 and with 5 atoms of oxygen. An interesting isomorphous relation exists between the members of the sulphur and those of the phosphorus group; sulphur being isomorphous with arsenicum, as is shown in the correspondence in form between crystals of iron pyrites, FeS_2, and those of mispickel, FeSAs.

The following table exhibits some of the corresponding compounds of the 5 triads just mentioned.

A gradation of properties is observed in these elements, and particularly in the three intermediate ones; phosphorus is the least dense, the most fusible and volatile; next follows arsenicum, and then antimony, in the order of their atomic weights. The acid properties of the oxidized compounds are more marked in nitrogen, than in phosphorus; they are weaker in arsenicum, still weaker in antimony, and are scarcely apparent in bismuth. The compounds with hydrogen follow the same order: ammonia is a powerful base and requires a high temperature for its decomposition, phosphuretted hydrogen is a very feeble base: in

arseniuretted hydrogen the basic character is not perceived, although manifest in some of its derivatives, and the same thing is true of antimony; each of these three hydrides being more easily decomposed by simple exposure to heat than the preceding one, whilst the attraction of bismuth for hydrogen is so feeble that its hydride is anknown.

H_3N Ammonia.	H_3P Phosphuretted hydrogen.	H_3As Arseniuretted hydrogen.	H_3Sb Antimoniuretted hydrogen.	
Cl_3N Nitrous chloride.	Cl_3P Phosphorous chloride.	Cl_3As Arsenious chloride.	Cl_3Sb Antimonious chloride.	Cl_3Bi Bismuth chloride.
	Cl_5P Phosphoric chloride.		Cl_5Sb Antimonic chloride.	
N_2O_3 Nitrous anhydride.	P_2O_3 Phosphorous anhydride.	As_2O_3 Arsenious anhydride.	Sb_2O_3 Antimonious oxide.	Bi_2O_3 Bismuth sesquioxide.
N_2O_5 Nitric anhydride.	P_2O_5 Phosphoric anhydride.	As_2O_5 Arsenic anhydride.	Sb_2O_5 Antimonic anhydride.	Bi_2O_5 Bismuthic anhydride.

PHOSPHORUS: P=31.

Atomic vol. □, or ½; *Rel. wt.* 62; *Theoretic Density of Vapour*, 4·2904; *Observed Density of Vapour at* 500° (932° F.). 4·35; *Fusing-pt.* 44°·5 (112°·1 F.); *Boiling-pt.* 278° (532°·4 F.); *usually Triad, as in* H_3P; *frequently Pentad, as in* PCl_5; *Mol. Vol.* ⊏⊐; *Mol. wt.* P_4=124.

(498) Phosphorus was discovered by Brandt in 1669. It is never met with in nature in the uncombined state, but it occurs in small proportion as tricalcic diphosphate, Ca_32PO_4, as a constituent of the primitive and volcanic rocks, by the gradual disintegration of which it passes into the soil: from the soil it is extracted by plants, which accumulate it, particularly in their seeds, in quantity sufficient for the support of the various animals which they supply with food. In the animal system it is collected in large amount, and when combined with oxygen and calcium, in the form of calcic phosphate (*bone phosphate*, Ca_32PO_4), it forms the principal earthy constituent of the bones of the vertebrata. Phosphorus also appears to be essential to the exercise of the higher functions of the animal, since it exists as a never-failing ingredient in the substance of which the brain and nerves are composed. It is likewise contained in

albumin and in fibrin in small proportion, and is present in the form of alkaline and earthy phosphates in the urine and solid excrements of animals.

Extraction.—Phosphorus was originally prepared from the salts contained in urine, but it is now obtained almost exclusively from the bones of animals, or from native calcic phosphate. In order to prepare it, bones were formerly always burned to whiteness by calcining them in an open fire for some hours, but now the gelatin of the bones is first extracted by heating them, under pressure, with water; or the bones are distilled in closed vessels, the ammonia and volatile products are collected, whilst the bone black is employed in sugar-refining, and after it has become useless for this purpose, it is burned in the open fire. Three parts of powdered bone-ash obtained by any of these methods are mixed with 2 of concentrated sulphuric acid, or 3 parts of crude acid of density 1·550, and 18 or 20 parts of water. The mixture after being allowed to stand for two or three days, is placed upon a strong linen filter, and the acid liquid is separated from the calcic sulphate by pressure; the residue is then washed with water, and the washings are added to the filtered solution. In this process the sulphuric acid is added in such quantity as partially to decompose the calcic phosphate; two-thirds of the calcium are removed by it as insoluble calcic sulphate, whilst the remaining third is left as an acid salt, in combination with the whole of the phosphoric acid. This latter compound is readily soluble in water, and is frequently described as *superphosphate of lime* (calcic-tetrahydric diphosphate; $H_4Ca_2P_2O_8$). The reaction may be thus expressed in symbols:

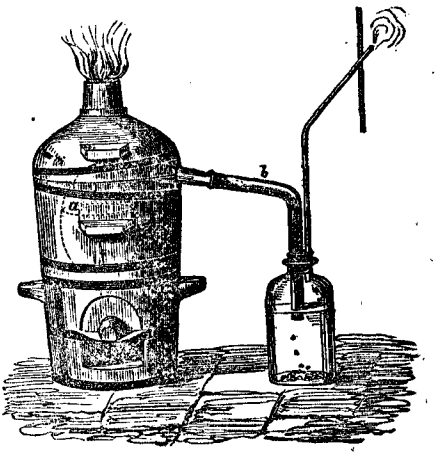
$$\underset{\text{Tricalcic phosphate.}}{Ca_3P_2O_8} + \underset{\text{Sulph. acid.}}{2H_2SO_4} = \underset{\text{Acid calcic phosphate.}}{H_4Ca_2P_2O_8} + \underset{\text{Calcic sulphate.}}{2CaSO_4}.$$

$$[P_2O_2(O_2Ca)''_3 + SO_2(OH)_2 = P_2O_2(OH)_4(O_2Ca)'' + 2SO_2(O_2Ca)''].$$

The acid solution is evaporated to the consistence of a syrup, then mixed with from one-fourth to one-half its weight of charcoal, and heated to incipient redness in an iron pot, stirring constantly. The mass, whilst hot, is transferred to an earthen retort (*a*, fig. 329), covered externally with a thin paste, consisting of a mixture of equal parts of borax and fire-clay, with a view of rendering it less porous. It is then gradually heated to full redness, when the phosphorus rises in vapour, and is condensed in the wide copper tube, *b*, dipping into the water contained in the receiver. This vessel is provided with a smaller

tube, open at both ends, for conveying away the uncondensed gases to a chimney. In this operation it is found necessary to convert the normal phosphate into superphosphate of calcium, since bone-ash, when heated, does not part with its phosphorus. The superphosphate, when heated, is decomposed into water and calcic metaphosphate; the latter being acted upon by the charcoal, reproduces tricalcic phosphate, which remains in the retort, whilst carbonic oxide and phosphorus pass off in the gaseous condition. Gaseous matters escape, therefore, during the whole operation, which may be regarded as consisting of two stages, the first being the decomposition of the superphosphate into calcic metaphosphate:

FIG. 329.



$$H_4Ca_2PO_4 = Ca_2PO_3 + 2OH_2;$$
$$[P_2O_2(OH)_4(O_2Ca)'' = P_2O_4(O_2Ca)'' + 2OH_2.]$$

whilst the second stage consists of the decomposition of the calcic metaphosphate; phosphorus, tricalcic phosphate, and carbonic oxide being produced:

$$3Ca_2PO_3 + 10C = P_4 + Ca_3{}_2PO_4 + 10CO.*$$
$$[3P_2O_4(O_2Ca)'' + 10C = P_4 + P_2O_2(O_2Ca)''_3 + 10CO.]$$

With a view to render the phosphorus perfectly pure, it is fused under warm water, with a solution of bleaching powder, and squeezed through wash-leather; or it may be fused, first under ammonia, and then under a solution of potassic dichromate in dilute sulphuric acid. The easy fusibility of phosphorus enables it to be moulded into sticks with facility; it is melted under water and run into tubes, in which it is allowed to solidify.

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* Phosphorus may also be obtained by heating an intimate mixture of charcoal and tricalcic phosphate or of bone-ash to bright redness in a current of hydrochloric acid gas, carbonic oxide and hydrogen being liberated along with vapour of phosphorus whilst calcic chloride is formed:

$$2(Ca_3{}_2PO_4) + 16C + 12HCl = P_4 + 16CO + 6H_2 + 6CaCl_2.$$

Properties.—Phosphorus is a soft, semi-transparent, colourless, waxy-looking solid, which, however, becomes hard and brittle at low temperatures. It may be obtained in brilliant transparent crystals by sealing it up in an exhausted glass tube, and leaving it for some weeks in a dark place. It fumes in the air, emitting white vapours of an alliaceous odour. It has a density of 1·83676 (Pisati and De Franchis); 1·83 at 10° (50° F.) (Schrötter). It fuses at 44°·5 (112°·1 F.), and if melted under an alkaline liquid and allowed to cool, it will long continue fluid at ordinary temperatures if undisturbed, but when touched with a wire or a glass rod it suddenly solidifies. Phosphorus is a non-conductor of electricity, both in the solid and in the liquid state. It is extremely inflammable, taking fire in the open air at a temperature very little above its fusing-point. If it contains impurities, such as oxide of phosphorus, it takes fire still more easily; so that great caution is required in handling it. It is better always to cut it under water, as the burns occasioned by melted phosphorus are deep and often extremely severe, from the difficulty of extinguishing the flame.

Phosphorus burns with a brilliant white flame, and emits dense white fumes of phosphoric anhydride. In closed vessels it boils at 278° (532°·4 F.) (Pisati and De Franchis), giving off a colourless vapour, of which 100 cubic inches, calculated at 30 inches Bar. and 60 F., would weigh about 135 grains. An atom of phosphorus, therefore, gives off a volume of vapour equal to one-half that of an atom of hydrogen; and, according to Deville, no appreciable alteration in the relative volumes of the two is effected by a temperature of 1040° (1904° F.). Phosphorus is insoluble in water, only slightly soluble in ether, but more so in benzene, in oil of turpentine, and in the fixed and essential oils. It is also freely dissolved by chloride of sulphur, by phosphorous chloride, and by carbonic bisulphide: when its solution in the bisulphide is allowed to fall upon filter-paper in the open air, the finely divided phosphorus left on the evaporation of the solvent absorbs oxygen so rapidly that it takes fire. If the solution be allowed to evaporate slowly in a current of hydrogen or carbonic anhydride, the phosphorus may be obtained crystallized in rhombic dodecahedra.

The vapour of phosphorus when mixed with hydrogen gives to the gas the property of burning with a green flame, which when examined spectroscopically exhibits two intense green lines, one of which appears to coincide with one of the lines of barium:

common amorphous phosphorus, hypophosphites, and phosphites, when introduced into Marsh's apparatus, give rise to this phenomenon, which is sufficiently sensitive to serve as a qualitative test of the presence of phosphorus. Phosphorus is acted on by a solution of ammonia with production of a black or green substance, which, according to Commaille (*Compt. Rend.*, 1869, lxviii. 263), has the composition P_3H; dry gaseous ammonia has no action on phosphorus.

Phosphorus is always preserved under water, for when exposed to the air, at all temperatures above 0° (32° F.) it gradually combines with oxygen, and undergoes a slow combustion, attended with the production of the white fumes and the garlic odour already mentioned; in a darkened room, a pale greenish light may be observed (hence its name, from φῶς, light, φορὸς, bearing). The luminosity of phosphorus is prevented by the admixture of certain inflammable vapours and gases in minute quantity with the atmosphere; if air be mixed with either $\frac{1}{450}$ of its bulk of olefiant gas, $\frac{1}{1820}$ of naphtha vapour, or $\frac{1}{4444}$ of vapour of oil of turpentine, a stick of phosphorus no longer appears luminous when exposed to its action (Graham).

It is remarkable that in oxygen the luminosity is not observed until the temperature rises to 15° (59° F.), unless the gas be rarefied, or be diluted with some other gas.

(499) **Different modifications of Phosphorus.**—Phosphorus assumes several different forms under the influence of causes apparently trifling. The *transparent* variety has been already mentioned; this, when kept exposed to light under water, assumes a second form, consisting of small plates; it then appears to be *white* and opaque, and is somewhat less fusible. It has a density of 1·515: white phosphorus becomes reconverted into the vitreous variety by a temperature not exceeding 50° (122° F.). A *black* variety of phosphorus was obtained by Thénard, and subsequently by Blondhot, by rapidly distilling phosphorus in a current of hydrogen; on cooling, it solidified to a black mass. It is very probable, however, that the presence of arsenic in the hydrogen might be the cause of this, since Ritter (*Compt. Rend.*, 1874, lxxviii. 192) and Blondhot (*ibid.*, lxxviii. 1130) have shown that a minute quantity of arsenic is capable of producing this effect. Traces of mercury also seem to give similar results. A fourth or *viscous* modification, analogous to viscous sulphur, may be obtained by heating very pure phosphorus to near its boiling-point and suddenly cooling it. A fifth form occurs in

the shape of *red* scales, which are obtained by the spontaneous sublimation of phosphorus in the Torricellian vacuum when exposed to the rays of the sun.

Red or Amorphous Phosphorus.—This red form of phosphorus has been carefully studied by Schrötter (*Ann. Chim. Phys.*, 1848, [3], xxiv. 406), who prepares it by the action of heat on ordinary phosphorus; for this purpose the dry phosphorus is introduced into a flask from which the air is displaced by means of a current of carbonic anhydride, and to the neck of which a long narrow tube, bent downward, is attached; the open end of this tube dips into a little mercury to prevent access of atmospheric air to the interior of the flask. Heat is next applied to the flask by means of an oil-bath; the phosphorus melts readily, and by maintaining the heat for 30 or 40 hours steadily between 230° and 240° (446° and 464° F.), almost all the phosphorus becomes converted into the solid amorphous variety. When the operation appears to be terminated, the apparatus is allowed to cool: carbonic bisulphide is then poured upon the mass in the flask, and allowed to stand for some hours: this is poured off, and fresh bisulphide added, the digestion being repeated so long as any phosphorus is dissolved, which may be known by allowing a few drops of the decanted liquid to evaporate spontaneously in a watch-glass; any dissolved phosphorus will be left behind.

The red powder of which the undissolved portion consists, takes fire spontaneously when exposed to the air, if not quite free from unaltered phosphorus; but does not do so if quite pure. The higher the temperature at which the transformation is effected, the deeper is the colour of the product, which in the finest specimens rivals that of vermilion. By heating the phosphorus more strongly during its preparation, the change may be produced much more rapidly, but the phosphorus then assumes the form of reddish-brown friable masses, with a conchoidal fracture. The process is not unattended with danger, however; for if the red powder be heated up to the point at which its re-conversion into the transparent variety takes place, the whole mass suddenly passes back into the ordinary form, with great development of heat, accompanied by the sudden formation of a large volume of phosphorus vapour. The change into the red modification, moreover, is never complete, a certain portion remaining unconverted; the proportion of this, when the transformation takes place, under pressure, at temperatures above the boiling-point of phosphorus, appears to be dependent on the vapour tension (Lemoine, *Compt. Rend.*, 1871, lxxiii. 797, 837,

and 990: Troost and Hautefeuille, *ibid.*, 1873, lxxvi. 76, 219; and 1874, lxxviii. 748); the change of red into ordinary phosphorus, or *vice versâ*, going on until a certain vapour tension is attained (which varies according to the temperature employed), and then the transformation ceases.

Amorphous phosphorus is manufactured on the large scale by heating the phosphorus at 240° (464° F.) in iron vessels which are closed all but a very small opening: all danger of explosion is thus avoided, and after the burning phosphorus has removed the oxygen from the enclosed air, there is but little loss, as diffusion takes place very slowly through the small aperture. The purification from ordinary phosphorus may be effected by grinding the mass to fine powder under water and boiling it with a solution of caustic soda as long as phosphuretted hydrogen is formed. The residual red phosphorus is then thoroughly washed from sodic hyposulphite, and afterwards dried. The changes produced in phosphorus by heat may be readily watched by placing a few fragments of well-dried phosphorus in a tube, upon which two or three bulbs have been blown, then expelling the air by a current of carbonic anhydride, and sealing one end of the tube,—the open end being made to dip into mercury. On applying heat to the phosphorus it becomes red, but on continuing to raise the temperature it distils over in colourless transparent drops, which ultimately solidify to a transparent colourless mass, although they frequently remain liquid for some hours.

Red or *amorphous phosphorus*, as it is commonly called, has been obtained distinctly crystallized in rhombohedrons, and differs remarkably in many of its properties from the waxy-looking stick phosphorus. It may be exposed to the air without emitting any odour. It absorbs oxygen slowly, however, the oxidation being more rapid if the powder be moist: phosphorus and metaphosphoric acids are formed, and from their deliquescent nature the powder becomes damp. This oxidation occurs so slowly that it was at first imagined that amorphous phosphorus underwent no change by exposure to the air. The density of amorphous phosphorus exceeds that of the vitreous form, the red powder, according to Brodie, having a density of 2·14; the crystals, however, have a density of 2·34 at 15° (59° F.). It is not soluble either in carbonic bisulphide, phosphorous trichloride, or in benzene. It may be heated in the open air without change until the temperature reaches 260° (500° F.); at this point it melts and bursts into flame, burning with the dazzling brilliancy of common phosphorus and emitting dense fumes of phosphoric anhydride.

Chlorine acts directly upon red phosphorus without the application of heat: the temperature rises, but the phosphorus does not take fire. When rubbed with potassic chlorate it detonates, very slight friction being sufficient to produce the effect: peroxide of manganese and peroxide of lead act in a similar way, but less readily.

The principal consumption of phosphorus is in the manufacture of lucifer matches. In the usual mode of preparing these matches, the ends of the pieces of wood are first dipped in melted paraffin, or are gummed and dusted over with sulphur, and then tipped with a mixture, in which the chief ingredients are an emulsion of phosphorus in glue, and potassic chlorate or black oxide of manganese. The manufacture is attended with considerable danger, from the highly inflammable and explosive nature of the ingredients used; but in addition to this risk those employed in the business are liable to a distressing form of caries of the lower jaw, arising from the action of the fumes of phosphorus when inhaled. Of these evils, the first is greatly lessened, and the second altogether avoided, by the use of amorphous phosphorus. An ingenious plan for diminishing the risk of fires from the use of lucifer matches consists in separating the phosphorus from the other combustible ingredients; a mixture of amorphous phosphorus with half its weight of powdered glass is attached by means of size to the rubbing surface for kindling the matches; whilst the matches themselves are tipped with a composition consisting of a mixture of potassic chlorate, antimonious sulphide, and powdered glass; these take fire when rubbed upon the phosphorized surface, but not by moderate friction upon any other substance, as they do not contain any phosphorus.

Although vitreous phosphorus acts as a powerful irritant poison when taken internally, the amorphous variety may be swallowed with impunity; the vitreous phosphorus forms the active ingredient in the phosphorus paste frequently used to destroy cockroaches and other kinds of vermin.

Owing to its strong attraction for oxygen, phosphorus reduces some of the soluble compounds of the metals to the metallic state; a stick of phosphorus placed in a solution of auric chloride or of argentic nitrate becomes speedily encased in reduced gold or silver. Salts of palladium, and copper, are also reduced gradually when a stick of phosphorus is immersed in their solutions. Ammoniacal solutions of nickel and cadmium heated with phosphorus give black precipitates containing phosphides of the metals (Oppenheim, *Deut. chem. Ges. Ber.*, 1872, v. 979).

(500) **PHOSPHIDES OF HYDROGEN.**—None of the compounds of phosphorus with hydrogen is possessed of acid characters: these compounds are four in number: viz., PH_3, PH_2, P_2H, and P_3H. The first is gaseous, the second liquid, and the other two are solid, at ordinary temperatures.

(501) **Phosphine**: *Phosphamine: Phosphuretted hydrogen gas: Phosphorous trihydride*; $PH_3=34$; *Rel. wt.* 17; *Theoretic*

Density, 1·1764; *Observed*, 1·214 (Dumas); *Atomic and Mol. Vol.* [ ]:

Preparation.—Phosphuretted hydrogen is very often prepared by heating fragments of phosphorus with a strong solution of potassic hydrate, or with cream of lime; hypophosphite of the metal is then formed, with evolution of spontaneously inflammable phosphuretted hydrogen; P_4+3OH_2+3KHO becoming $3KPH_2O_2+PH_3$ [$P_4+3OH_2+3OKH=3POH_2(OK)+PH_3$]. When potassic hydrate is used, free hydrogen to the amount of 15—35 per cent. is also evolved, owing to the gradual decomposition of the hypophosphite when boiled with excess of free alkali, a phosphate being formed. If an alcoholic solution of potash be substituted for the aqueous one, the gas is no longer spontaneously inflammable, but is far from pure. Better results are obtained by decomposing calcic phosphide with water, the evolved gas only containing about 13 per cent. of free hydrogen, whilst if hydrochloric acid be used instead of water the proportion of hydrogen is reduced to 6 per cent. Phosphuretted hydrogen gas may also be obtained by the decomposition of phosphorous acid by heat; $4H_2PHO_3$ yielding $3H_3PO_4+PH_3$ [$4POH(OH)_2=PH_3+3PO(OH)_3$]; but even this is contaminated with about 6 per cent. of hydrogen; hypophosphorous acid gives an analogous result, $2HPH_2O_2$ becoming $H_3PO_4+PH_3$ [$2POH_2(OH)=PH_3+PO(OH)_3$].

Pure phosphine may be prepared from phosphonic iodide, by the action of water, or even better, a solution of potassic hydrate, the reaction being $PH_4I+KHO=PH_3+KI+OH_2$. The most convenient way of conducting the operation is to place a quantity of phosphoric iodide in pieces, about the size of a pea, in a flask closed with a cork and provided with a delivery tube and dropping bulb; the solution of potassic hydrate (density about 1·27) is allowed to drop in gradually from the bulb tube by means of a stopcock, whilst the evolved gas passes off through the delivery tube. About one litre of the gas is obtained from 7·3 grams of the iodide by this process. The gas obtained by the action of potassic hydrate on phosphorus has the remarkable property of taking fire spontaneously in atmospheric air or in oxygen gas; if allowed to escape into the air in bubbles, each bubble as it breaks produces a beautiful white wreath of phosphoric anhydride, composed of a number of ringlets revolving in vertical planes around the axis of the wreath itself, as it ascends; thus tracing before the eye, with admirable distinctness, the rapid gyratory movements communicated to the air contained in a bubble, when

it is allowed to burst upon the surface of a still sheet of water. If the bubbles be allowed to rise into a jar of oxygen, a brilliant flash of light, attended with a slight concussion, accompanies the bursting of each bubble. Owing to the spontaneous inflammation of the gas, it should be made in small vessels containing but little atmospheric air. Graham has shown that the addition of small quantities of the vapour of some inflammable bodies, such as ether, naphtha, and oil of turpentine, destroys this self-lighting power; and that porous bodies, such as charcoal, also remove it. On the other hand, the gas obtained from phosphorous acid and from phosphonic iodide, is not self-lighting, but the addition of so small a quantity as $\frac{1}{10,000}$ of its bulk of the vapour of nitrous anhydride confers this property upon it.

Properties.—Phosphuretted hydrogen is a highly inflammable colourless gas, with a very disagreeable alliaceous odour, liquefiable under pressure; it is slightly soluble in water, and when passed through solutions of certain metallic salts such as those of lead, copper, or mercury, it is absorbed and decomposed; phosphides of the metals are produced and are precipitated. Those of lead and copper are black, that of mercury is yellow. Solutions of the salts of gold and silver are reduced to the metallic state and phosphoric acid is found in solution. When the gas is pure, it is wholly absorbed by a solution of chloride of lime. It is decomposed by sulphurous acid, as well as by chlorine, bromine, and iodine; the gas taking fire immediately if brought in contact with chlorine or bromine water or with fuming nitric acid. A mixture of the gas with air or with oxygen explodes at a temperature of 150° (302° F.), or sometimes even at the ordinary temperature, if the pressure be suddenly diminished. In this gas, half a volume of the vapour of phosphorus and 3 volumes of hydrogen are condensed into the space of 2 volumes. Its composition may therefore be thus represented:

				By weight.		By vol.
Phosphorus	P	=	31	or 91·18	...	0·5
Hydrogen	H_3	=	3	8·82	...	3·0
Phosphuretted hydrogen	H_3P	=	34	100·00	...	2·0

The combining volume of phosphuretted hydrogen is the same as that of ammonia, to which it is analogous in composition. It also splits up into its elements almost as easily as ammonia on passing electric sparks through the gas, and a similar decomposition takes places under the influence of the silent discharge, but it is not so complete, the reaction according to Berthelot being,

$4PH_3 = 5H_2 + P_4H_2$. It is without action upon either red or blue litmus. Some indication of a basic character is, however, shown by it, for it combines with certain of the acids in definite proportions; for example, it combines with hydriodic acid, forming phosphonic iodide, $PH_3.HI$ or, PH_4I.

Phosphuretted hydrogen combines with the perchlorides of many of the metals, such as those of tin, titanium, antimony, and iron. These compounds are decomposed by water, with escape of phosphuretted hydrogen gas.

(502) **Liquid Phosphide of Hydrogen**: PH_2, or P_2H_4 (P_5H_{10} ?) $\left[P''_2H_4 = \begin{Bmatrix} PH_2 \\ PH_2 \end{Bmatrix}\right]$.—The singular property which phosphuretted hydrogen possesses, in certain cases, of igniting spontaneously when mixed with free oxygen, long remained without explanation, as a careful analysis indicated little or no difference in composition between the self-lighting gas and the other variety, which does not possess this property. The true cause of the phenomenon was, however, traced some years ago by P. Thénard to the presence of a minute quantity of the vapour of another phosphide of hydrogen, P_2H_4, which takes fire the instant that it comes in contact with uncombined oxygen (*Ann. Chim. Phys.*, 1854, [3], xiv. 5). This compound exists at ordinary temperatures as a volatile liquid, which by exposure to light is decomposed into a yellow, solid, and but slightly inflammable phosphide, P_2H, and into the non-self-lighting gas, PH_3; for $P_5H_{10} = P_2H + 3PH_3$ $\left[5'P_2''H_4 = \begin{Bmatrix} P(P'''H)'' \\ P(P'''H)'' \end{Bmatrix}^{?} + 6PH_3\right]$. It had long been remarked, that when the spontaneously inflammable gas was exposed to the sunlight for a few hours, a solid yellow compound was deposited in small quantity upon the sides of the vessel, whilst the gas lost its self-lighting power; and that this power was also destroyed by exposing the gas to a great degree of cold. This effect is evidently due, in the case of the exposure to sunlight, to decomposition of the inflammable compound, and in the case of the application of cold, to its condensation in the liquid form.

Liquid phosphide of hydrogen may be prepared by conducting the gas which is disengaged by the action of water upon phosphide of calcium, Ca_2P_2, through a bent tube immersed in a freeing-mixture of ice and salt: a colourless liquid of high refracting power is thus condensed, which does not solidify at $-20°$ ($-4°$ F.). It takes fire the instant that it comes into contact with air, and burns with the intense white light of phosphorus. Solar light quickly decomposes it into the solid phosphide, P_2H or P_4H_2, and into the gaseous phosphuretted hydrogen. If a little of the vapour of this liquid be allowed to diffuse itself through hydrogen, carbonic oxide, or any other combustible gas, it confers upon it the property of taking fire spontaneously when mixed with atmospheric air or with oxygen.

(503) **Solid Phosphides of Hydrogen** ? P_2H.—The liquid phosphide is immediately decomposed by hydrochloric acid, and the solid yellow phosphide of hydrogen is formed. This substance is readily prepared by treating phosphide of calcium with hot hydrochloric acid. Rüdorff (*Zeits. Chem.*, 1866, ii. 637) states that when phosphorous diiodide, PI_2, is added to hot water, phosphorine, PH_3, is given off whilst a yellow phosphide of the composition P_2H is left identical with that obtained from the liquid phosphide. It is not soluble either

in water or in alcohol, and when heated with a solution of potassic hydrate it dissolves with liberation of phosphuretted hydrogen gas. There appear to be two varieties of the solid phosphide, one of a yellow, the other of a green colour; they do not differ from each other in composition. The solid yellow hydride of phosphorus takes fire at about 150° (302° F.).

As already mentioned (p. 287) the action of an aqueous or alcoholic solution of ammonia on phosphorus gives rise to a solid phosphide of hydrogen, to which Commaille has assigned the formula P_3H, and which is black or green according to the circumstances under which it has been formed. It does not give off gas when boiled with water; nitric acid acts strongly on it at the ordinary temperature, but it does not take fire like the compound HP_2. It throws down a phosphide of copper, from a solution of the sulphate of that metal.

(504) **CHLORIDES OF PHOSPHORUS.**—With chlorine, phosphorus forms two compounds, a trichloride, PCl_3, and a pentachloride, PCl_5. So strong is the chemical attraction between these elements, that phosphorus immediately takes fire in an atmosphere of chlorine. The following table shows the composition of these chlorides, and of two of their derivatives:

		In 100 parts.			
		Phosph.	Chlorine.	Oxygen.	Sulphur.
Trichloride of phosphorus	$PCl_3 = 137{\cdot}5$	22·54	77·46		
Pentachloride „	$PCl_5 = 208{\cdot}5$	14·86	85·14		
Oxytrichloride „	$POCl_3 = 153{\cdot}5$	20·19	69·38	10·43	
Sulphotrichloride „	$PSCl_3 = 169{\cdot}5$	18·28	62·84		18·88

(505) **TRICHLORIDE, *or* TERCHLORIDE OF PHOSPHORUS;** *Phosphorous chloride*; $PCl_3 = 137{\cdot}5$; *Density of Vapour, Theoretic*, 4·7575; *Observed*, 4·79; *of Liquid*, 1·6129 *at* 0° (32° F.); *Boiling-pt.* 76° (168° 8 F.); *Mol. Vol.* [ ]; *Rel. wt.* 68·75.—This liquid is sometimes prepared by causing the vapour of phosphorus to pass over corrosive sublimate placed in a long tube and gently heated; but it may be obtained more conveniently by passing a gentle stream of perfectly dry chlorine gas over dry and melted phosphorus contained in a retort; it is better, however, to use amorphous instead of ordinary phosphorus. The operation may be conducted in the same manner as in the preparation of chloride of sulphur (fig. 319); the trichloride distils as a very volatile, transparent, colourless, fuming liquid. It dissolves phosphorus freely, and is itself soluble in benzene and in carbonic bisulphide: alcohol and ether decompose it with evolution of great heat, giving rise to various organic compounds. It is also immediately decomposed by a large excess of water, and forms phosphorous and hydrochloric acids; $PCl_3 + 3OH_2$, yielding

H_3PHO_3+3HCl [$PCl_3+3OH_2=POH(OH)_2+3HCl$]. Trichloride of phosphorus absorbs chlorine with avidity, and is converted into the pentachloride; at a boiling temperature it also absorbs oxygen and furnishes the oxytrichloride.

(506) **PENTACHLORIDE OR PERCHLORIDE OF PHOSPHORUS**; *Phosphoric chloride;* $PCl_5=208\ 5$; *Theoretic Density of Vapour,* 7·214; *Observed,* 7·226; *Rel. wt.* 52·1; *Mol. Vol.* [redacted].—This compound* is obtained by placing dry phosphorus in a flask provided with a stopcock, exhausting the air, and allowing chlorine to enter so long as it is absorbed; or it may be formed by treating trichloride of phosphorus in a large glass flask with an excess of chlorine. Pentachloride of phosphorus is also now prepared on a considerable scale by dissolving phosphorus in carbonic bisulphide and passing dried chlorine in excess through the solution which is cooled artificially during the operation; on evaporating the solution the pentachloride is obtained in a crystalline state. It forms a white crystalline solid, which volatilizes below 100° (212° F.) whilst still solid, but it may be fused under pressure at a temperature of 148° (298°·4 F.). It combines readily with ammonia, and burns in the flame of a lamp, producing chlorine and phosphoric anhydride. It is very deliquescent, and is immediately decomposed by a large excess of water into phosphoric and hydrochloric acids; PCl_5+4OH_2 forming H_3PO_4+5HCl [$PCl_5+4OH_2=PO(OH)_3+5HCl$]. Phosphoric pentachloride unites with the chlorides of many other metals, as with antimonic pentachloride, $SbCl_5.PCl_5$, molybdic perchloride, $MoCl_4.PCl_5$, and ferric chloride, $Fe_2Cl_6.2PCl_5$ (Cronander, *Deut. chem. Ges. Ber.*, 1873, vi. 1466).

(507) **BROMIDES OF PHOSPHORUS.**—*A Tribromide,* PBr_3 [*Density* at 0° (32° F.), 2·925; *Boiling-pt.* 175°·3 (347°·5 F.)], *Pentabromide* and *Oxybromide* of phosphorus, analogous to the corresponding compounds with chlorine, may be formed by similar methods; the last mentioned forms crystals which melt at 46° (114°·8 F.), and boil at 195° (383° F.).

(508) **Phosphorous Bromochlorides.**—Several of these compounds have been obtained by the action of bromine on phos-

* The vapour density of this compound was formerly supposed to be anomalous, but Wurtz (*Compt. Rend.*, 1873, lxxvi. 601) has found from determinations of the density of the vapour of the pentachloride diffused through that of the trichloride that it is 7·226. It would seem that the pentachloride vapour decomposes when heated alone, partially dissociating at a comparatively low temperature into chlorine and the trichloride; if, however, the atmosphere in which dissociation takes place is already saturated with the vapour of the trichloride this dissociation is prevented.

phorous trichloride. The trichloride and bromine, mixed in the proportions PCl_3 and Br_2 and exposed to a low temperature for some time, unite to form a crystalline compound of the formula PCl_3Br_2. At 35° (95° F.) it is resolved into two layers of liquid, the lower of which is the darkest. On now dropping in a crystal of PCl_3Br_2 into the lower layer, it yields a mass of large dark red crystals of the composition PCl_3Br_4 (Michaelis, *Deut. chem. Ges. Ber.*, 1872, v. 9). Prinvault (*Compt. Rend.*, 1872, lxxiv. 868) by the action of bromine on phosphorous trichloride, has obtained a compound PCl_3Br_8, crystallizing in needles which melt at 25° (77° F.), and may be distilled at 90° (194° F.) without decomposition. Above 90° (194° F.) it decomposes, yielding a very unstable compound, PCl_2Br_7. This heated with phosphorous trichloride yields a phosphoric bromochloride of the formula PCl_4Br. He has also obtained a compound PCl_3Br_4 by the direct action of phosphorous chloride with the compound PCl_3Br_8. It is most probable that all the compounds containing more bromine than those formed on the type PCl_5 are molecular combinations.

(509) **IODIDES OF PHOSPHORUS.**—Two iodides of phosphorus may be formed, viz., a diiodide and a triiodide (Corenwinder, *Ann. Chim. Phys.*, 1850, [3], xxx. 242). *The Diiodide*, $PI_2=285$, may be prepared by dissolving 1 part (or 1 atom) of phosphorus in carbonic bisulphide, and adding 8¼ parts (or 2 atoms) of iodine; on cooling the mixture artificially, thin flexible prismatic crystals of the iodide are deposited, of a bright orange colour. This iodide melts at 110° (230° F.), and is decomposed by water, yielding hydriodic acid and other products.

Phosphorous iodide, or *Triiodide of phosphorus*, $PI_3=412$.—This compound may be obtained in a manner similar to the last, by dissolving 1 part of phosphorus and 12½ parts of iodine in carbonic bisulphide. When the solution is concentrated by evaporation, and subsequently cooled by a freezing mixture, dark red, six-sided plates of the iodide are formed; these melt between 50° and 55° (122° and 131° F.), and on cooling crystallize again in fine prisms. It deliquesces rapidly when exposed to the air.

Brodie (*Jour. Chem. Soc.*, 1852, v. 289) finds that iodine, when heated with phosphorus in the proportion of 1 atom of iodine to 100 atoms of phosphorus, converts nearly the whole of the phosphorus into the red variety described by Schrötter. When phosphorus was placed in a long tube, and heated until it just melted, and iodine was projected gradually into the phos-

phorus, the iodine was dissolved, colouring the phosphorus slightly red; when heated by an oil-bath at 100° (212° F.), the colour became deep red; and between 120° and 130° (248° and 266° F.), a scarlet powder was deposited on the sides of the tube; at 140° (284° F.), the mass was quite solid, and on raising the heat to 200° (392° F.), a sharp explosion took place: a sudden evolution of heat occurred, and the cork which closed the tube was blown out by the vapour of phosphorus. The red mass may be distilled in closed tubes, and when it is condensed in the cooler portions of the tubes it is still in the red modification. The changes which occur in the process are supposed to be the following: first, the formation of diiodide of phosphorus; next, the transformation of this iodide by heat into an allotropic iodide; and thirdly, the decomposition of this new iodide into red phosphorus and a volatile iodide, which acts upon a further portion of the phosphorus; and thus the action is indefinitely continued.

(510) **PHOSPHONIUM IODIDE**, $PH_4I = 162$: *Density of Vapour; Observed*, 2·77.—Equal volumes of hydriodic acid and phosphine, PH_3, unite without condensation to form this compound. It may be easily prepared by introducing into a small retort 127 parts of dry iodine ground up with powdered glass, and 31 of phosphorus in small fragments, then adding 20 parts of water; the vapours which come off consist of phosphonic iodide mixed with an excess of hydriodic acid. It condenses in crystals in the neck of the retort if it is kept cool. Hofmann (*Deut. chem. Ges. Ber.*, 1873, vi. 291) dissolves 40 parts of iodine in its own weight of carbonic bisulphide, and adds 68 of iodine, then distils off the bisulphide, and gradually adds 24 parts of water by means of a dropping tube. The retort containing the iodide of phosphorus is connected with a globe receiver by means of a long, wide, glass tube, and this again with two wash-bottles, the first containing dilute hydriodic acid, and the second water, a gentle current of carbonic anhydride being passed through the apparatus during the whole operation. As soon as the water begins to act on the iodide, hydriodic acid and phosphonic iodide are produced, the latter subliming and forming crystalline crusts in the wide tube and receiver, whilst the hydriodic acid is absorbed in the wash-bottles. Phosphonic iodide crystallizes in cubes. It fuses at a moderate heat, and if air be excluded may be sublimed without alteration. The crystals are deliquescent, and as already noticed are decomposed by water into hydriodic acid and phosphine (p. 291). A corresponding bromide has been obtained.

(511) **PHOSPHORIC PENTAFLUORIDE**, $PF_5 = 126$.—This compound has been obtained by Thorpe (*Proc. Roy. Soc.*, 1876, xxv. 122), by the action of phosphoric pentachloride on arsenic trifluoride, thus:

$$3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3.$$

It is a colourless pungent gas which fumes strongly in the air, and is decomposed by water into hydrofluoric and phosphoric acids. It does not liquefy at 7° (44°·6 F.) under a pressure of 12 atmospheres. It is non-inflammable, and is unchanged by the passage of the electric spark. With dry ammonia, it unites to form the compound $2PF_5.5NH_3$, which is soluble in water.

(512) **PHOSPHAM** (HN_2P ?).—If phosphorous chloride be cooled by a freezing mixture, and saturated with ammoniacal gas, a white saline mass, $5NH_3.PCl_3$, is obtained; it is to be introduced into a tube of Bohemian glass, and heated to redness in a current of dry carbonic anhydride as long as any ammonic chloride is sublimed: a yellowish-white, bulky, amorphous powder remains behind; this substance is Rose's *phosphide of nitrogen*; but there can be no doubt that it contains hydrogen; it is the *phospham* of Gerhardt, and perhaps its composition may be represented by the formula given above, although it is somewhat doubtful if it is a definite compound. In closed vessels it sustains a red heat without fusion or volatilization, but when heated in the air it is slowly oxidized, with formation of phosphoric anhydride; if projected into fused potassic hydrate, it is decomposed with incandescence, tripotassic phosphate being formed, whilst ammonia and nitrogen are disengaged: but it is remarkable that dry chlorine and hydrochloric acid gases, and the vapour of sulphur, have no action on it, even at a red heat; and it is but very slowly attacked by concentrated nitric acid. Solutions of the alkalies exert scarcely any action upon it. When heated in hydrogen, ammonia is formed. It combines with sulphuretted hydrogen, and if heated in a current of this gas, the new compound as it is formed is slowly sublimed in the form of a white powder.

Schiff states (*Zeits. Chem.*, 1869, v. 609) that when *perfectly dry* ammonia is passed into phosphoric oxychloride, the mass powdered and again treated with ammonia until saturated, a mixture of *phosphotriamide*, $PO(NH_2)_3$, and ammonic chloride is obtained, from which the latter may be removed by washing with water. Phosphotriamide is a snow-white, amorphous powder, which is scarcely attacked by long-continued boiling with water, alkaline solutions, or dilute acids; concentrated sulphuric acid dissolves it at a gentle heat, and the solution contains ammonia and phosphoric acid. Fused with potassic hydrate, it yields a phosphate with evolution of ammonia. If, in the preparation of the triamide, oxychloride is used which contains pentachloride, some *phosphodiamide*, $PO(NH)_2H$, will be formed.

By the action of ammonia on phosphoric oxychloride, Gladstone obtained the amides $P(NH_2)Cl_2O$ and $P(NH_2)_2ClO$, and these when heated with water gave rise to phosphamic acids. Of these the following have been obtained and analysed:

Phosphamic acid	$P_2(NH_2)H_3O_6$
Phosphodiamic acid	$P_2(NH_2)_2H_2O_5$
Phosphotriamic acid	$P_2(NH_2)_3HO_4$
Tetraphosphodiamic acid	$P_4(NH_2)_2(OH)_4O_7$
Tetraphosphotetramic acid	$P_4(NH_2)_4(OH)_2O_7$

(Gladstone, *Jour. Chem. Soc.*, 1864, 225; 1865, 1; 1866, 1 and 290; and Salzmann, *Deut. chem. Ges. Ber.*, 1874, vii. 494).

(513) **OXIDES AND ACIDS OF PHOSPHORUS.**—Only two compounds of phosphorus and oxygen are known, viz.:

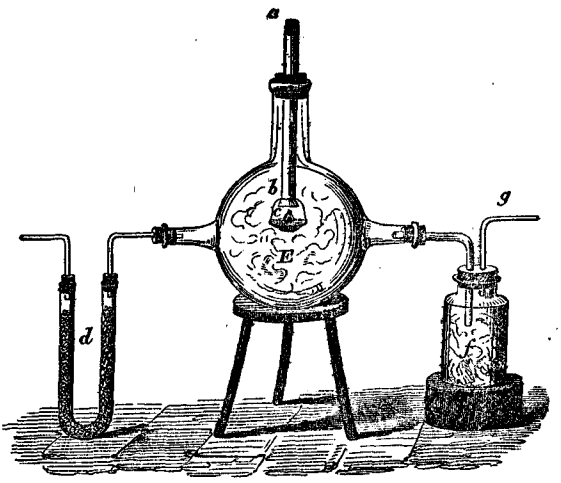
		In 100 parts.	
		Phosphorus.	Oxygen.
Phosphorous anhydride	$P_2O_3 = 110$	56·36	43·64
Phosphoric anhydride	$P_2O_5 = 142$	43·66	56·34

Phosphorus forms four oxidized acids, which are respectively monobasic, dibasic, and tribasic, in proportion as the quantity of oxygen increases: these acids are the following:

Hypophosphorous acid (monobasic)	HPH_2O_2	$[POH_2(OH)]$
Phosphorous acid (dibasic) . . .	H_2PHO_3	$[POH(OH)_2]$
Hypophosphoric acid (dibasic) . .	H_2PO_3	
Phosphoric acid (tribasic) . . .	H_3PO_4	$[PO(OH)_3]$

(514) **PHOSPHORIC ANHYDRIDE**: $P_2O_5 = 142$.—The most important of the oxides of phosphorus is that which unites with water to form phosphoric acid; it occurs native in considerable quantity in the form of tricalcic diphosphate, $Ca_3 2PO_4$. The anhydride of this acid is the sole product of the rapid combustion of phosphorus in dry oxygen or in atmospheric air. By means of the apparatus shown in fig. 330, a large quantity of phosphoric anhydride may be readily obtained in a few hours: E is a three-necked globe, in the centre of which is suspended a porcelain dish, *c*; this dish is attached by means of platinum wire to the wide tube *a b*, which is closed at *a* with a cork; the bottle, *f*, is connected by the tube *g*, with an aspirator, or other convenient means of maintaining a continuous current of air through the apparatus: the air as it enters is thoroughly dried by passing over pumice moistened with sulphuric acid, contained in the tube, *d*. A fragment of well dried phosphorus in placed in the dish, *c*, and kindled by touching it with a hot wire. As the phosphorus burns away fresh pieces are introduced through the aperture *a*, which is immediately closed with the cork after each addition. When large quantities

FIG. 330.



are required phosphoric anhydride may be conveniently made in a sheet-iron cylinder furnished with a cover and resting in a funnel of the same material as recommended by Graboffski (*Ann. Chem. Pharm.*, 1865, cxxxvi. 119). The phosphorus is burned in a copper spoon supported by an arm passing through an opening in the side of the cylinder. The short wide neck of the funnel allows the anhydride to be shaken into a bottle placed there for its reception. The atmosphere should be dry when the operation is performed, as there is no provision for drying the air. The anhydride obtained in this way generally contains traces of one of the lower oxides of phosphorus. It forms a snow-white, flocculent, non-crystalline, anhydrous, and extremely deliquescent, powder, which fuses at an elevated temperature, and may be sublimed by a heat approaching to whiteness. It does not emit vapour at ordinary temperatures. When dropped into water it combines with it, emitting a hissing noise; the greater part is instantly dissolved, leaving a few gelatinous flocks, which slowly disappear; $P_2O_5 + 3OH_2 = 2H_3PO_4$. After it has once been dissolved, it cannot again be converted into the anhydride by the application of heat, as the whole compound is then gradually dissipated in vapour. Owing to its powerful attraction for water, phosphoric anhydride is often used as a desiccating and dehydrating agent, and for this purpose it surpasses in efficacy almost every known subtance: it should be stored in well-stoppered bottles, or better, in hermetically sealed glass flasks.

(515) **PHOSPHORIC ACID.**—The pure acid is generally procured in a hydrated state, by boiling 1 part of phosphorus in 13 parts of nitric acid of density 1·20. The phosphorus becomes oxidized by the nitric acid, which is decomposed with escape of nitric oxide, whilst the phosphoric acid remains dissolved in the dilute acid; it is advisable to use amorphous phosphorus, as the oxidation takes place much more rapidly than with ordinary phosphorus. The addition of a very small quantity of bromine or iodine also greatly facilitates the action. When the phosphorus has all disappeared, the excess of nitric acid is expelled by evaporating the liquid in a platinum vessel until dense white fumes begin to arise; on cooling, the acid solidifies to a transparent glassy mass, frequently termed *glacial phosphoric acid.* This glacial acid is extremely deliquescent, producing a solution, which has a density of 2·0 when saturated. It is intensely acid, but not caustic.

The oxidation of phosphorus by nitric acid furnishes an easy means of ascertaining the composition of phosphoric anhydride.

For this purpose 3·1 grams of phosphorus are boiled in a glass retort with pure dilute nitric acid. The greater part of the excess of water and nitric acid having been distilled off, the acid solution is added to 35 grams of plumbic oxide, in a weighed platinum dish: the liquid is slowly evaporated, and the residue ignited; by a red heat the whole of the nitric acid is expelled, and the phosphoric anhydride alone remains in combination with the oxide of lead. The oxide and anhydride together will be found to weigh 42·1 grams, showing an increase in weight upon the phosphorus and oxide of lead of 4·0 grams: 31 parts of phosphorus therefore require 40 parts of oxygen for conversion into phosphoric anhydride.

A less pure acid is obtained on adding to a solution of superphosphate of lime (prepared from bones by the process already described as a preliminary step towards procuring phosphorus) ammonic sesquicarbonate until effervescence ceases; tricalcic diphosphate is precipitated, leaving triammonic phosphate in solution. The precipitated calcic phosphate is separated by filtration, the liquid evaporated to dryness, and the residue ignited. Ammonia is expelled, and phosphoric acid (contaminated with all the soluble salts which the bones contained) remains behind. The following table gives the strength of aqueous solutions of pure phosphoric acid at 15°·5 (60° F.) (J. Watts, *Chem. News*, 1865, xci. 160):

Density.	P_2O_5 in 100 parts.	Density.	P_2O_5 in 100 parts.	Density.	P_2O_5 in 100 parts.
1·508	49·60	1·328	36·15	1·144	17·89
1·492	48·41	1·315	34·82	1·136	16·95
1·476	47·10	1·302	33·49	1·124	15·64
1·464	45·63	1·293	32·71	1·113	14·33
1·453	45·38	1·285	31·94	1·109	13·25
1·442	44·13	1·276	31·03	1·095	12·18
1·434	43·95	1·268	30·13	1·081	10·44
1·426	43·28	1·257	29·16	1·073	9·53
1·418	42·61	1·247	28·24	1·066	8·62
1·401	41·60	1·236	27·30	1·056	7·39
1·392	40·86	1·226	26·36	1·047	6·17
1·384	40·12	1·211	24·79	1·031	4·15
1·376	39·66	1·197	23·23	1·022	3·03
1·369	39·21	1·185	22·07	1·014	1·91
1·356	38·00	1·173	20·91	1·006	0·79
1·349	37·37	1·162	19·73		
1·339	36·74	1·153	18·81		

There are three different forms of phosphoric acid, each of which possesses the properties of a distinct acid: viz.:

Metaphosphoric acid . . .	HPO_3	$[PO_2(OH)]$
Orthophosphoric or ordinary phosphoric acid . . .	H_3PO_4	$[PO(OH)_3]$
Pyrophosphoric acid . . .	$H_4P_2O_7$	$\left[P_2O_3(OH)_4 = \begin{Bmatrix} PO(OH)_2 \\ O \\ PO(OH)_2 \end{Bmatrix}\right]$

These different forms of the acid retain their peculiar characteristics when dissolved in water, and form salts with 1, with 3, or with 4 equivalents of metal, according as the metaphosphoric, the orthophosphoric, or the pyrophosphoric acid is employed. Owing to the important influence which the study of these combinations has exercised upon the theory of saline combinations in general, it will be necessary to examine them somewhat in detail.

(516) **Orthophosphoric** (from ὀρθός, right) or **Tribasic Phosphoric Acid**, *Trihydric Phosphate*; H_3PO_4.—If the liquid formed by dissolving the glacial acid in water be boiled for some time, and sodic carbonate be then added until the solution becomes slightly alkaline, a tribasic hydric disodic phosphate is obtained, which on evaporation crystallizes in large transparent rhombic prisms of the formula, $Na_2HPO_4.12OH_2$. If this solution be mixed with a neutral solution of argentic nitrate, a canary-yellow precipitate of triargentic phosphate, Ag_3PO_4, is formed. Although this solution was neutral or slightly alkaline before admixture with argentic nitrate, it will be found afterwards to have a decidedly acid reaction upon litmus, nitric acid having been liberated:

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$

$$[PO(OH)(ONa)_2 + 3NO_2(OAg) = PO(OAg)_3 + 2NO_2(ONa) + NO_2(OH).]$$

Plumbic acetate, $(C_2H_3O_2)_2Pb$, may be used as a precipitant instead of argentic nitrate, and in this case a white triplumbic diphosphate, Pb_32PO_4, is thrown down. If this phosphate of lead be well washed, suspended in water, and exposed to the action of a current of sulphuretted hydrogen, black insoluble plumbic sulphide is formed, whilst pure orthophosphoric acid is liberated and remains dissolved in the liquid;

$$Pb_32PO_4 + 3SH_2 = 2H_3PO_4 + 3PbS.$$

The plumbic sulphide may be removed by filtration, and the acid obtained in deliquescent, hard, brittle, prismatic, transparent crystals, by evaporation *in vacuo* over sulphuric acid. The action of phosphoric oxychloride on orthophosphoric acid gives rise to metaphosphoric acid, $2H_3PO_4 + POCl_3 = 3HPO_3 + 3HCl$, or pyro-

phosphoric acid, $5H_3PO_4 + POCl_3 = 3H_4P_2O_7 + 3HCl$, according to the proportion of oxychloride employed. Phosphorus pentachloride and trichloride, under similar circumstances, yield metaphosphoric acid, and also, in the case of the trichloride, phosphorous acid. The orthophosphoric is a tribasic acid; and therefore it requires 3 atoms of a monad metal for saturation. The salts of this hydrate form the *orthophosphates* or common *tribasic phosphates.*

There are three varieties of these salts, which may be indicated by general formulæ as follows:

1 Trimetallic phosphates . . .	M_3PO_4	$[PO(OM)_3]$
2 Hydric dimetallic phosphates .	M_2HPO_4	$[PO(OH)(OM)_2]$
3 Dihydric metallic phosphates .	MH_2PO_4	$[PO(OH)_2(OM)]$

It is not necessary that the 3 equivalents of basyl should consist of the same metal in these salts; two or even three different basyls may coexist in the same salt; as, for example, in microcosmic salt which is *sodic ammonic hydric phosphate* $NH_4NaHPO_4.4OH_2$: $[PO(ONa)(ONH_4(OH).4OH_2)]$.

In the first class, the 3 atoms of hydrogen in the acid have been displaced by 3 of a metal, as, for example, in the trisodic phosphate, $Na_3PO_4.12OH_2$; these salts, when soluble, have a strongly alkaline reaction: in the second class, 2 atoms of the basic hydrogen have been displaced by 2 of a metal; they are analogous to the ordinary rhombic hydric disodic phosphate, $Na_2HPO_4.12OH_2$: the soluble salts of this class are neutral, or have a feebly alkaline reaction: whilst the third class contains only 1 atom of metal with 2 of basic hydrogen; they are of the form of the sodic dihydric phosphate, $NaH_2PO_4.OH_2$, formerly called the biphosphate of soda; these salts have a strongly acid reaction, and are often spoken of as the *superphosphates.*

Tests.—The soluble orthophosphates are characterized by yielding with argentic nitrate a yellow precipitate of triargentic phosphate in neutral solutions; this is freely soluble both in nitric acid and in ammonia. They also yield a crystalline precipitate on adding a clear solution of magnesic sulphate rendered alkaline by ammonia, and stirring briskly; this precipitate, which consists of $Mg''NH_4PO_4.6OH_2$, $[P_2O_2(O_2Mg)_2(ONH_4)_2.12OH_2]$ is insoluble in water containing free ammonia; when ignited, the water and ammonia are expelled, and it becomes converted into dimagnesic pyrophosphate, $Mg_2P_2O_7$, a compound frequently employed as a means of estimating the amount of phosphates in solutions which contain them: 100 parts of the ignited residue

corresponding to 63·96 of P_2O_5.* Neutral solutions of the orthophosphates give precipitates with salts of barium and calcium; the tribaric and tricalcic diphosphates are readily soluble in acetic acid; but free phosphoric acid gives no precipitate in solutions of the nitrates of calcium, barium, or silver, or in a solution of ferric chloride: when ammonic molybdate is added to a solution of a phosphate acidulated with nitric acid, a characteristic yellow precipitate of ammonic molybdophosphate is formed; the deposition of this precipitate is favoured by heating the liquid.

The quantity of phosphoric acid in a solution may be ascertained, if neither sulphuric nor hydrochloric acid be present, by means of plumbic acetate; the solution, before this salt is added to it, should be neutralized by ammonia, and then strongly acidulated with acetic acid; the precipitate, $PbHPO_4$, should be well washed and ignited, by which means it is rendered anhydrous; 100 parts of the ignited residue represent 24·15 of P_2O_5. Chancel has shown that the acid solution of bismuth trinitrate, $Bi'''3NO_3$, furnishes an admirable method of separating phosphoric acid from many metals, such as iron, calcium, and aluminium, which form phosphates soluble only in acidulated liquids. Care is requisite to remove any chlorine or sulphuric acid from the liquid, before adding the solution of bismuth, which is prepared by dissolving 1 part of the crystallized nitrate in 4 parts of nitric acid of density 1·36, adding 30 parts of water, then boiling, and filtering if necessary. In separating the bismuth phosphate by this reagent, the liquid must be boiled, and the precipitate well washed with boiling water and carefully dried: 100 parts of bismuth phosphate, $BiPO_4$, correspond to 23·28 of phosphoric anhydride, P_2O_5. With ferric salts, phosphoric acid forms an insoluble buff-coloured precipitate of ferric orthophosphate, $FePO_4.2OH_2$, which is also sometimes employed to estimate the quantity of phosphoric acid in a solution.

(517) **Pyrophosphoric Acid**; *Tetrahydric Pyrophosphate*, $H_4P_2O_7$. — When hydric disodic (rhombic) phosphate, $Na_2HPO_4.12OH_2$, is heated, it first melts in its water of crystallization, which gradually evaporates and leaves a hard, white, saline mass; this consists of Na_2HPO_4 and may be redissolved in water with all its former properties provided the temperature has not exceeded 150° (302° F.). If, however, it be heated to redness before redissolving, 2 molecules of the salt coalesce to form a new salt, whilst 1 molecule of water is expelled; $2Na_2HPO_4$ becoming $Na_4P_2O_7+OH_2$: $[2PO(OH)(ONa)_2=OH_2+P_2O_3(ONa)_4$ or $\begin{bmatrix}PO(ONa)_2\\O\\PO(ONa)_2\end{bmatrix}$; on redissolving the residue in water and evaporating the solution, the liquid no longer furnishes rhombic,

* The arseniates give precipitates both with ammoniacal salts of magnesium and of molybdic acid, similar to those furnished by the phosphates.

but acicular crystals of a tetrasodic phosphate having the composition $Na_4P_2O_7.10OH_2$; and the solution instead of yielding a yellow precipitate with argentic nitrate, now gives a white one, consisting of $Ag_4P_2O_7$. In this case, the solution, if neutral to litmus before the addition of the silver salt, behaves differently from one of sodic orthophosphate, as it remains neutral afterwards, because no free acid is liberated:

$$4AgNO_3 + Na_4P_2O_7 = 4NaNO_3 + Ag_4P_2O_7.$$

With a solution of plumbic acetate, sodic pyrophosphate also yields a white precipitate, the composition of which is represented by the formula $Pb_2P_2O_7$; and if the lead salt be suspended in water, and decomposed with sulphuretted hydrogen, it yields a solution of pyrophosphoric acid, $H_4P_2O_7$. The excess of sulphuretted hydrogen must be got rid of by exposure to the air (not by heat, otherwise the acid assimilates water and becomes converted into the tribasic acid $H_4P_2O_7 + OH_2 = 2H_3PO_4$, and the pyrophosphoric acid may then be obtained in crystals by evaporation *in vacuo* over sulphuric acid. Tetra-sodic phosphate, from the mode in which it is obtained, is usually termed the *pyrophosphate* of sodium, and the corresponding salts of the acid, *pyrophosphates* (from $\pi\tilde{\upsilon}\rho$, fire). No solid pyrophosphate of potassium or ammonium can be obtained; these salts are stable whilst in solution, but on evaporation they become converted into tribasic phosphates by the assimilation of water (Graham). Pyrophosphoric acid appears to be tetra-basic: and forms two classes of salts; one with four atoms of a fixed basyl, with the formula $M_4P_2O_7$ like the ordinary sodic pyrophosphate, $Na_4P_2O_7.10OH_2$; the other containing 2 atoms of hydrogen and 2 of a univalent metal, $M_2H_2P_2O_7$, corresponding in composition to the acid pyrophosphate of sodium, or disodic dihydric pyrophosphate:

$$Na_2H_2P_2O_7.$$

Neutral solutions of the pyrophosphates also give, in solutions of calcic and baric salts, white precipitates of the pyrophosphates of the metals; salts of nickel and copper, when mixed with a solution of sodic pyrophosphate, yield double salts containing 2 atoms of sodium to 3 of the other metal:

$$2Na_4P_2O_7 + 3Cu''2NO_3 = Cu''_3Na_22P_2O_7 + 6NaNO_3.$$

Double salts of the alkali-metals with manganese, zinc, and iron have also been prepared and analyzed.

When sodic pyrophosphate is heated with sulphuric acid until acid vapours are no longer given off, and the product

crystallized from dilute phosphoric acid, *sodic phosphosulphate*, $Na_2SO_4HPO_3.OH_2$, is obtained in brilliant plates. It is decomposed by water into a sulphate and free phosphoric acid.

(518) **Metaphosphoric Acid**; *Hydric Metaphosphate*, HPO_3. —If, in preparing the rhombic, or hydric disodic phosphate (516), two equal portions of phosphoric acid be taken, and after neutralizing one portion with sodic carbonate, as above directed, the second quantity of acid be added to the neutralized solution, a tribasic, sodic dihydric phosphate, consisting of NaH_2PO_4, will be obtained on evaporating the liquid to dryness; but on igniting the residue, the two atoms of hydrogen will be expelled in the form of water, and a fusible monobasic phosphate of sodium, or *sodic metaphosphate*, $NaPO_3$, will remain in the form of a transparent glass. This, if dissolved in water, gives with argentic nitrate a gelatinous white precipitate of *argentic metaphosphate*, $AgPO_3$, different in appearance and composition from either of the former phosphates of silver; it is soluble in excess of the sodium salt. With plumbic acetate a white precipitate also is formed, $Pb2PO_3$: it is fusible in boiling water, and when decomposed with sulphuretted hydrogen it yields the corresponding acid, HPO_3, distinguished from the other hydrates by its power of coagulating the albumin of white of egg. It also gives white precipitates with baric chloride and argentic nitrate. Acetic acid does not coagulate albumin, neither does a solution of sodic metaphosphate; but if the two solutions be mixed, the acetic acid liberates metaphosphoric acid, and the albumin becomes coagulated. Tribasic phosphoric acid loses water by prolonged heating to redness, the glassy residue being converted almost entirely into metaphosphoric acid. Sodic metaphosphate is capable of uniting with water of crystallization, which it retains if dried at 100° (212° F.): this water is not basic, for on again dissolving the salt, it gives the usual reactions of the metaphosphates. If, however, the salt be heated to 150° (302° F.), it does not lose weight, but becomes converted into the disodic dihydric pyrophosphate, the water having now changed its function in the salt, from its hydrogen having become basic (Graham):

$$2NaPO_3.OH_2 \text{ becomes } Na_2H_2P_2O_7.$$

Hydrated sodic metaphosphate. — Pyrophosphate of sodium and hydrogen.

This change of properties in the salt, without any alteration in the proportions of its components, thus admits of a satisfactory explanation; and it is a striking and instructive illustration of

the facility with which chemical compounds, by a change in molecular constitution, may give rise to substances whose properties may be very different, although their percentage composition may be the same.

Sodic metaphosphate forms with salts of barium a white insoluble *baric metaphosphate*, Ba_2PO_3, which gradually dissolves when boiled, assimilating 2 molecules of water, and becoming converted into the tribasic, baric tetrahydric diphosphate, $BaH_4{}_2PO_4$. Metaphosphoric acid is monobasic and the solutions of its salts redden litmus feebly.

Metaphosphoric acid, when boiled in aqueous solution, becomes converted into the ordinary tribasic acid, so that it cannot be concentrated by the application of heat, $HPO_3 + OH_2$ becoming H_3PO_4: the solution may be preserved, however, for a short time at the ordinary temperature without change.

The following table furnishes a synoptic view of some of the principal phosphates, metaphosphates, and pyrophosphates:

I. ORTHOPHOSPHATES. M_3PO_4; M_2HPO_4; MH_2PO_4.

Trisodic phosphate	$Na_3PO_4.12OH_2$	$[PO(ONa)_3.12OH_2]$
Hydric disodic (rhombic) phosphate	$Na_2HPO_4.12OH_2$	$[PO(OH)(ONa)_2.12OH_2]$
Sodic dihydric (acid) phosphate	$NaH_2PO_4.OH_2$	$[PO(OH)_2(ONa).OH_2]$
Microcosmic salt	$NaNH_4HPO_4.4OH_2$	$[PO(OH)(ONa)(ONH_4).4OH_2]$
Calcic phosphate (native) ...	$Ca''_3{}_2PO_4$	$[P_2O_2(O_2Ca)''_3]$
Dicalcic phosphate	$Ca''_2H_2{}_2PO_4.3OH_2$	
Superphosphate of calcium ...	$Ca''H_4{}_2PO_4$	$[P_2O_2(OH)_4(O_2Ca)'']$
Ammonic magnesic phosphate	$Mg''NH_4.PO_4.6OH_2$	
Zincic phosphate	$Zn''_3{}_2PO_4.5OH_2$	
Ferric phosphate	$Fe'''PO_4.2OH_2$	
Triplumbic phosphate ...	$Pb''_3{}_2PO_4$	
Bismuthic „ ...	$Bi'''PO_4$	
Triargentic „ (yellow)...	Ag_3PO_4	

II. METAPHOSPHATES. MPO_3.

Sodic metaphosphate ...	$NaPO_3$	$[PO_2(ONa)]$
Plumbic „	$Pb''2PO_3$	$[P_2O_4(O_2Pb)'']$
Argentic „	$AgPO_3$	$[PO_2(OAg)]$

III. PYROPHOSPHATES. $M_4P_2O_7$; $MM'_3P_2O_7$.

Sodic pyrophosphate... ...	$Na_4P_2O_7.10OH_2$
Magnesic pyrophosphate (precip.)	$Mg''_2P_2O_7.5OH_2$
Zincic pyrophosphate ...	$Zn''_2P_2O_7.5OH_2$
Plumbic „	$Pb''_2P_2O_7$
Cupric „	$Cu''_2P_2O_7.5OH_2$
Pyrophosphate of copper and sodium	$Cu''_3Na_2{}_2P_2O_7$
Argentic pyrophosphate ...	$Ag_4P_2O_7$

Fleitmann and Henneberg (*Ann. Chem. Pharm.*, 1848, lxv. 324) have described two classes of salts which are probably anhydro-phosphates. By melting sodic pyrophosphate and sodic metaphosphate together, in the proportion of 1 molecule of the pyrophosphate and 2 of the metaphosphate, they obtained a salt, *a*, consisting of $2Na_3PO_4.P_2O_5$; and by fusing 8 molecules of the metaphosphate with 1 of the pyrophosphate, a definite sodium salt, *b*, was obtained which consisted of $4Na_3PO_4.3P_2O_5$; both these salts are very unstable, and in solution pass quickly into a mixture of pyrophosphate and metaphosphate. Definite salts of silver and of magnesium corresponding to these compounds were obtained.

Fleitmann and Henneberg propose to represent these various classes of salts as follows, comparing quantities of each which contain equal amounts of metallic basyl, the quantity of phosphoric anhydride successively increasing in each series:

Orthophosphates	$6M_2O.2P_2O_5$	or	$4M_3PO_4$
Pyrophosphates	$6M_2O.3P_2O_5$		$3M_4P_2O_7$
Fleitmann and Henneberg, *a*	$6M_2O.4P_2O_5$		$2M_6P_4O_{13}$
Ditto ditto ... *b*	$6M_2O.5P_2O_5$		$M_{12}P_{10}O_{31}$
Metaphosphates	$6M_2O.6P_2O_5$		$12MPO_3$

in which case the pyrophosphates, as well as the salts discovered by Fleitmann and Henneberg, would be compounds of the orthophosphates with different proportions of a metaphosphate. A pyrophosphate, for example, may be represented thus: $Na_3PO_4.NaPO_3 = Na_4P_2O_7$; the salt *a* being $Na_3PO_4.3NaPO_3 = Na_6P_4O_{13}$, and the salt *b* being $Na_3PO_4.9NaPO_3 = Na_{12}P_{10}O_{31}$.

Modifications of Metaphosphoric Acid.—If the ordinary or glassy sodic metaphosphate be fused and allowed to cool very slowly, it furnishes a beautiful crystalline mass, and this, when dissolved in a small quantity of hot water, forms a liquid which divides into two strata; the smaller of these contains unchanged sodic metaphosphate; but the bulk of the liquid is a solution of the crystalline salt of *trimetaphosphoric acid*, which may be obtained on evaporation in oblique rhombic prisms of the formula $Na_3P_3O_9.6OH_2$: the solution of this salt is *neutral* and has a cooling saline taste, whilst that of the ordinary or vitreous metaphosphate is insipid. The crystalline salt, by boiling, is rapidly converted into the *acid* orthophosphate or sodic dihydric phosphate, NaH_2PO_4. A beautifully crystallized silver salt, consisting of $Ag_3P_3O_9.OH_2$, may be obtained from the crystalline sodium salt by precipitation, and a similar lead salt, $Pb''_32P_3O_9.3OH_2$, has also been prepared.

Maddrell (*Proc. Chem. Soc.*, 1847, p. 273) has described a series of monobasic metaphosphates which are anhydrous, crystalline, and insoluble in water, but soluble in oil of vitriol. They were formed by evaporating a solution of the sulphate or nitrate of the metal with an excess of phosphoric acid, and heating until the sulphuric or other acid of the salt was expelled. Salts of potassium, sodium, aluminium, copper, nickel, and others were thus obtained. The sodium salt, if prepared with phosphoric acid which contains magnesium, or any metal isomorphous with magnesium, forms an insoluble double metaphosphate: the magnesium double salt is crystalline, and consists of $(Mg2PO_3)_3.2NaPO_3$. These different varieties of metaphosphates are supposed to be due to the existence of several polymeric varieties of metaphosphoric acid, but the subject needs further investigation.

(518*a*) **HYPOPHOSPHORIC ACID**, H_2PO_3.—According to Salzer (*Ann. Chem. Pharm.*, 1877, clxxxvii. 322) this acid is contained together with phosphorous and phosphoric acids in Pelletier's 'phosphatic acid,'—the syrupy liquid formed when phosphorus is allowed to oxidize slowly in contact with

moist air,—and is also produced by the action of air on phosphorous acid. It may be separated from the other acids with which it is associated by taking advantage of the sparing solubility of the acid sodic salt. A solution of hypophosphoric acid may be easily obtained by suspending plumbic hypophosphate in water, and decomposing it with sulphuretted hydrogen; it is colourless, strongly acid, and may be boiled without undergoing change, but when evaporated to a syrupy consistence it is resolved into phosphorous and phosphoric acids. It is unacted on by chromic acid or hydric peroxide, but is oxidized to phosphoric acid by potassic permanganate, slowly in the cold, rapidly when heated.

Hypophosphoric acid is dibasic, and forms two classes of salts of the general formula, $MHPO_3$ and M_2PO_3; they have a general resemblance to the phosphites and hypophosphites, but are much more stable. *Sodic hydric hypophosphate*, $NaHPO_3.3OH_2$, crystallizes in colourless oblique rhombic prisms, which are soluble in 45 parts cold, and 5 of boiling water; when strongly heated it leaves sodic metaphosphate. *Disodic hypophosphate*, $Na_2PO_3.5OH_2$, crystallizes in needles which require about 30 parts of cold water for solution. *Plumbic hypophosphate*, $PbPO_3$, is obtained as a white precipitate on adding a lead salt to an aqueous solution of the hydric sodic salt. It is insoluble in acetic acid, but soluble in dilute sulphuric acid.

(519) **PHOSPHOROUS ANHYDRIDE**, P_2O_3, may be prepared by burning phosphorus with a limited supply of dry air: a white, volatile, deliquescent, inflammable powder, destitute of crystalline structure, is thus obtained, which consists of the anhydride mixed with small quantities of oxide of phosphorus and phosphoric anhydride.

Phosphorous Acid; *Dihydric phosphite*, H_2PHO_3, may be obtained in solution by passing a stream of chlorine very slowly through a deep layer of phosphorus melted under water, so that each bubble of gas shall be completely absorbed by the phosphorus; phosphorous chloride, PCl_3, is formed, and is immediately decomposed by the water into hydrochloric and phosphorous acids: $PCl_3 + 3OH_2 = H_2PHO_3 + 3HCl$: $[PCl_3 + 3OH_2 + POH(OH)_2 + 3HCl]$. If the acid liquid be concentrated by a heat not exceeding 200° (392° F.), hydrochloric acid is expelled, and the acid is obtained in deliquescent rectangular prisms, H_3PO_3, which melt at 74° (165°·2 F.). It gradually absorbs oxygen from the air, and is decomposed by a high temperature into phosphoric acid and phosphuretted hydrogen: $4H_2PHO_3 = 3H_3PO_4 + PH_3$. It is also furnished in a less pure form, by the slow combustion which occurs when phosphorus is left exposed to the action of the atmosphere at the ordinary temperature; this may be safely effected by placing sticks of phosphorus in tubes open at both ends, the lower aperture of the tube being a little contracted so as to prevent the phosphorus from falling out; a number of these tubes are then placed in a funnel, and the dense acid liquid which is gradually formed drains into a vessel placed for its reception. In this process phosphorous anhydride is first produced; this being deliquescent attracts moisture from the air, and then, by gradually absorbing oxygen, it forms phosphoric acid, but the oxidation never proceeds so far as to convert the whole into phosphoric acid. The liquid consists of a mixture of phosphorous, hypophosphoric and phosphoric acids, which was at one time supposed to be a peculiar oxide of phosphorus, and was termed *phosphatic acid*. Bromine acts on crystallized phosphorous acid when the two are heated together in sealed tubes, metaphosphoric or orthophosphoric acid being produced according to the proportions employed:

$$H_3PO_3 + Br_2 = HPO_3 + 2HBr,$$
$$4H_3PO_3 + 3Br_2 = 3H_3PO_4 + 3HBr + PBr_3.$$

Phosphites.—Phosphorous acid is dibasic, and forms two classes of salts, the general formula of its normal salts being M_2PHO_3: [POH(OM)$_2$], whilst that of the acid phosphites is $M'HPHO_3$: [POH(OH)(OM)]. Normal sodic phosphite, for instance, consists of $Na_2PHO_3.5OH_2$; when heated to 300° (572° F.) the 5 molecules of water of crystallization are expelled. The acid phosphite of barium, dried at 100° (212° F.), consists of baric dihydric diphosphite, $BaH_2 2PHO_3$. The acid phosphites when heated emit hydrogen gas, whilst a metaphosphate remains behind; for example, $BaH_2 2PHO_3$ becomes $Ba2PO_3 + 2H_2$. The normal phosphites of the heavy metals when heated emit both hydrogen and phosphuretted hydrogen; for instance, plumbic phosphite:

$$5PbPHO_3 = Pb_3 2PO_4 + Pb_2P_2O_7 + PH_3 + H_2$$
$$[5POH(O_2Pb)'' = P_2O_2(O_2Pb)''_3 + P_2O_3(O_2Pb)''_2 + PH_3 + H_2].$$

Free phosphorous acid does not immediately reduce potassic permanganate, unless heated with it; a reaction which distinguishes it from hypophosphorous acid, which, even in the cold, rapidly discharges the colour of the permanganate in acid solutions. The normal phosphites of the alkali-metals are freely soluble, most others but sparingly so: amongst them plumbic phosphite is the least soluble; it is also insoluble in acetic acid. With a solution of mercuric chloride, $HgCl_2$, acidulated with acetic acid, the phosphites give a white precipitate of mercurous chloride (calomel), the formation of which is hastened by heating the liquid. Phosphorous acid in excess decolorizes solutions of cupric sulphate, cuprous sulphate being formed, but if the sulphate is in excess, metallic copper is precipitated on boiling for a short time:

$$3H_3PO_3 + CuSO_4 + 3OH_2 = Cu + 3H_3PO_4 + H_2SO_4 + 2H_2.$$

Another characteristic reaction of the phosphites is the reduction of sulphurous acid to sulphuretted hydrogen, with simultaneous precipitation of sulphur, owing to the action of the sulphuretted hydrogen on the excess of sulphurous acid:

$$3H_2PHO_3 + H_2SO_3 = 3H_3PO_4 + SH_2.$$

(520) **HYPOPHOSPHOROUS ACID**; *Hydric hypophosphite*, HPH_2O_2: [POH$_2$(OH)].—This compound was formerly considered to be an acid of phosphorus with a still smaller quantity of oxygen than the preceding, but its anhydride has never been obtained. A hypophosphite is produced when phosphorus is boiled with a solution of potassic or sodic hydrate, or with a hydrate of one of the alkaline earths. It may thus be prepared by Rose's method of boiling phosphorus with a solution of baric hydrate; phosphuretted hydrogen escapes, and on evaporation, a baric salt is obtained, of the formula $Ba2PH_2O_2$, formed by the reaction: $3BaH_2O_2 + 2P_4 + 6OH_2 = 3Ba2PH_2O_2 + 2PH_3$: [$3Ba(OH)_2 + 2P_4 + 6OH_2 = 3P_2O_2H_4(O_2Ba)'' + 2PH_3$]; on adding the requisite quantity of sulphuric acid, pure hypophosphorous acid is obtained in solution, whilst the barium is separated as sulphate. Baric hypophosphite may also be prepared by heating phosphorus with a solution of baric sulphide, when free hydrogen escapes mixed

with phosphuretted and sulphuretted hydrogen; the last traces of baric sulphide are removed by the addition of a little plumbic sulphate. On evaporating a solution of hypophosphorous acid, not allowing the temperature to rise above 105° (221° F.) until most of the water has been driven off, and then heating gradually to 135° (275° F.), an oily liquid is obtained which when cooled below 0° (32° F.), solidifies to a snow-white crystalline mass: The crystals melt at 17°·4 (63°·4 F.). According to Geuther and Pomidorf, however, it is converted into phosphorous acid at a temperature of 110° (230° F.), with evolution of phosphuretted hydrogen. Hypophosphorous acid solution has a sour, somewhat bitter taste, and gradually absorbs oxygen from the air, being converted into phosphorous acid: its acid properties are but feebly marked. When heated, it first loses water; and by a stronger heat is decomposed, emitting phosphuretted hydrogen, whilst phosphoric acid is formed; $2HPH_2O_2$ becoming $H_3PO_4+PH_3$: [$2POH_2(OH)=PO(OH)_3+PH_3$]. Owing to the partial decomposition of the phosphuretted hydrogen, a little phosphorus is generally deposited at the same time, and a corresponding quantity of hydrogen is liberated.

Hypophosphorous acid is distinguished from phosphorous acid by a remarkable reaction with the salts of copper; if to an excess of free hypophosphorous acid a solution of cupric sulphate be added, and the liquid be warmed to about 55° (131° F.), a solid insoluble hydride of copper, Cu_2H_2, is precipitated. On raising the liquid which contains the precipitate, to the boiling-point, this hydride is decomposed into hydrogen gas and metallic copper. Hydriodic acid acts powerfully on hypophosphorous acid with formation of phosphorous acid and phosphonic iodide: sulphuric acid oxidizes it to phosphorous acid with separation of sulphur, $2PO_2H_3+SO_2=H_3PO_3+S$: the sulphur, however, acts on a portion of the unattacked hypophosphorous acid and gives rise to sulphuretted hydrogen.

Hypophosphites.—The researches of Dulong, of Rose, and of Wurtz have shown that the hypophosphites are monobasic, consequently the acid forms but a single class of salts, of which the normal formula is

$$M'PH_2O_2 \quad [POH_2(OM)].$$

Sodic hypophosphite, for example, consists of $NaPH_2O_2$; the lead salt may be represented as $Pb_2PH_2O_2$. They correspond, therefore, to the monobasic phosphates, but 2 atoms of hydrogen have taken the place of 1 atom of oxygen in the radicle of the acid. The hypophosphites are all soluble in water; many of them crystallize easily, by the spontaneous evaporation of their solutions; the crystallized salts may be preserved unchanged, but when their solutions are evaporated at a high temperature, they are gradually converted into phosphites

by absorption of oxygen. Like phosphorous acid, they reduce gold and silver from their salts. The hypophosphites of the alkali-metals contain no water of crystallization: they are deliquescent, and soluble in alcohol.* Calcic hypophosphite, $Ca_2PH_2O_2$, requires about 6 parts of cold water for solution, and is scarcely more soluble in boiling water. Each molecule of the baric salt retains a molecule of water when crystallized at ordinary temperatures, but if crystallized from a boiling solution, it is deposited in anhydrous tables, $Ba_2PH_2O_2$. Magnesic hypophosphite, $Mg_2PH_2O_2.6OH_2$, crystallizes in brilliant, regular octohedra, which are efflorescent. The hypophosphites of zinc, nickel, cobalt, and iron, also retain $6OH_2$; those of sodium, lithium, strontium, and manganese retain but 1 molecule of water of crystallization, which they lose at 150° (302° F.). Those of potassium, ammonium, calcium, thallium, copper, and lead, contain no water of crystallization.

(521) **OXIDE OF PHOSPHORUS,** P_4O.—A still lower degree of oxidation of phosphorus is said to exist, which possesses neither acid nor alkaline properties. It is formed in small quantity when phosphorus is burned in air, and is one of the constituents of the yellow or red residue after the combustion has terminated. It is not, however, a compound of any importance, and is now generally regarded as amorphous phosphorus contaminated with a little phosphoric acid. It has neither smell nor taste, and is quite insoluble in water.

(522) **PHOSPHORYL CHLORIDE,** *Phosphoric oxytrichloride; or Oxychloride of phosphorus;* $POCl_3 = 153{\cdot}5$; *Rel. wt.* 76·75; *Density of Liquid,* 1·71185 at 0° (32° F.); *of Vapour, Theoretic,* 5·311; *Observed,* 5·298; *Boiling-pt.* 107°·2 (225° F.); *Mol. Vol.* [redacted].—This compound is formed when the vapour of water is allowed to mingle slowly with that of the pentachloride, hydrochloric acid and oxychloride of phosphorus being the result. The reaction is as follows: $PCl_5 + OH_2 = POCl_3 + 2HCl$. The oxychloride is a limpid, volatile, fuming liquid, which solidifies to a mass of crystals at a low temperature: these melt at 2°·5 (36°·5 F.). It is decomposed by water into phosphoric and hydrochloric acids. When heated with zinc at a high temperature in sealed tubes, a small portion of it is reduced to phosphorous trichloride PCl_3 (Thorpe).

Phosphoric oxytrichloride may be obtained with facility by Gerhardt's plan of distilling 1 part of crystallized boracic acid with 4½ parts of phosphoric chloride, when the following reaction occurs:

$$3PCl_5 + 2(HBO_2.OH_2) = 3POCl_3 + 6HCl + B_2O_3$$
$$[3PCl_5 + \quad 2B(OH)_3 = 3POCl_3 + 6HCl + \mathbf{B_2O_3}].$$

The oxychloride is readily condensed, whilst hydrochloric acid passes off in the form of gas, leaving boracic anhydride in the

* Sodic hypophosphite, which is now prepared largely for medicinal purposes, sometimes explodes spontaneously during the evaporation of its aqueous solution.

retort. Crystallized oxalic acid may be substituted for boracic acid in this operation, but it does not answer quite so well. The oxychloride may also be prepared by heating the pentachloride with phosphoric anhydride; $3PCl_5+P_2O_5=5POCl_3$; or by passing oxygen gas into boiling phosphorous trichloride.

Both the chlorides and the oxychloride of phosphorus have been extensively used in the preparation of various organic substitution-products, particularly the oxychlorides and anhydrides of the organic acids.

Oxychloride of phosphorus, when heated with boric anhydride at about 170° (338° F.) in sealed tubes for some hours, yields a white mass, and also a compound which sublimes into the upper portion of the tube in colourless crystals, having the composition $POCl_3.BCl_3$; this melts at 73° (163°·4 F.), but is at the same time decomposed. It is also formed by the action of boric trichloride on phosphoric oxytrichloride or phosphoric anhydride. The white mass above mentioned is probably a mixture of phosphoric anhydride and boric anhydride. When heated to redness, however, it forms the compound PBO_4 insoluble in water (Gustavson, *Deut. chem. Ges. Ber.*, 1871, iv. 975).

(523) **PYROPHOSPHORIC CHLORIDE**; $P_2O_3Cl_4=252$.—Another oxychloride of phosphorus has been obtained by Geuther and Michaelis (*ibid.*, 1871, iv. 766) by the action of nitric peroxide, N_2O_4, on phosphorous trichloride, cooled by a freezing mixture: nitrosyl chloride, NOCl, is given off, and the product, which also contains phosphoric anhydride, phosphoric oxytrichloride, and unaltered trichloride, is submitted to fractional distillation. The pure pyrophosphoric chloride is a colourless liquid, which boils at 210°—215° (410°—419° F.), but is at the same time partly decomposed into trichloride of phosphorus and phosphoric anhydride. Its density at 7° (44°·6 F.) is 1·58, and it does not solidify at −18° (−0°·4 F.). A compound of the formula PO_2Cl appears to be formed when a mixture of phosphoric anhydride and oxytrichloride is heated at 200° (392° F.), $POCl_3+P_2O_5=3PO_2Cl$. It is a thick syrupy mass.

(524) **SULPHIDES OF PHOSPHORUS.**—Sulphur and phosphorus may be melted together in all proportions, great heat being developed by their union; on this account the operation is usually effected under warm water, but the experiment requires to be conducted very carefully, in order to avoid explosion. Several definite compounds exist between them, corresponding in composition with the oxides of phosphorus; and in addition to these, a combination, P_2S_6, may be obtained

(Berzelius). The pentasulphide, P_2S_5, which is the compound of most practical importance, may be readily prepared by heating a mixture of powdered sulphur (160 parts) and amorphous phosphorus (62 parts) in a glass flask loosely covered, until the mass fuses. It may be obtained in transparent crystals by sublimation. All the sulphides of phosphorus are more fusible than either element separately, and are exceedingly inflammable; most of them can be obtained in crystals. They combine with the sulphides of the alkali-metals and form a series of definite salts.

(525) **PHOSPHORIC SULPHOTRICHLORIDE**, or *Sulphochloride of phosphorus*, $PSCl_3 = 169{\cdot}5$ [*Density of Liquid*, 1·6682 at 0° (32° F.); *of Vapour, Theoretic*, 5·8647; *Observed*, 5·878; *Mol. Vol.* [ ]; *Rel. wt.* 84·75; *Boiling-pt.* 125° (257° F.)], is a compound corresponding to the oxytrichloride, but containing sulphur instead of oxygen. It is obtained by decomposing phosphoric chloride with sulphuretted hydrogen; $PCl_5 + SH_2$, yielding $PSCl_3 + 2HCl$. It may be procured still more easily by the gradual addition of powdered antimonious sulphide to phosphoric chloride:

$$3PCl_5 + Sb_2S_3 = 3PSCl_3 + 2SbCl_3,$$

or by adding phosphorus to sulphur chloride in the proportions indicated by the equation $3S_2Cl_2 + P_2 = 2PSCl_3 + S_4$, and distilling the product: likewise by heating phosphoric pentasulphide with the pentachloride, $3PCl_5 + P_2S_5 = 5PSCl_3$; in a few minutes the mass liquefies, and on distillation the sulphochloride is obtained quite pure. Sulphotrichloride of phosphorus is a fuming colourless liquid of very pungent odour. If heated with a solution of sodic hydrate in excess, it exchanges its chlorine for oxygen; sodic chloride is formed, and a trisodic *sulphoxyphosphate* may be obtained in six-sided tabular crystals which contain $12OH_2$. The composition of this salt is analogous to that of the trisodic phosphate, but the two are not isomorphous. The following equation explains the changes which accompany its production (Wurtz):

$$PSCl_3 + 6NaHO = Na_3PSO_3 + 3NaCl + 3OH_2$$
$$[PSCl_3 + 6ONaH = PS(ONa)_3 + 3NaCl + 3OH_2].$$

Corresponding compounds with barium, calcium, and strontium may be formed by double decomposition with the sodium salt; they are white and insoluble.

(526) **SULPHOBROMIDES OF PHOSPHORUS.**—Several of these are known. The *pyrophosphoric sulphobromide*, $P_2S_3Br_4$, may be obtained by adding the requisite quantity of bromine to phosphorous trisulphide dissolved in carbonic bisulphide. It is an oily liquid of density 2·2621 at 17° (62°·6 F.). By distillation it is decomposed into *phosphoric orthosulphobromide*, $PSBr_3$, and phosphoric pentasulphide, $3P_2S_3Br_4 = 4PSBr_3 + P_2S_5$. The orthosulphobromide may be obtained by Baudrimont's method of acting on phosphoric pentabromide with sulphuretted hydrogen, but is more conveniently prepared by adding 8 parts of bromine to a well-cooled solution of 1 pt. of phosphorus and 1 of sulphur in carbonic bisulphide, and subsequent distillation. The first portion which passes over, consists of carbonic bisulphide, but the latter when treated with water yields a crystalline hydrate of the sulphobromide, $PSBr_3.OH_2$. This melts at 35° (95° F.), and is at the same time resolved into water and the sulphobromide; the latter may, however, be more readily obtained by drying the bisulphide solution of the hydrate with calcic chloride, and allowing it to evaporate. It forms a crystalline mass which melts at 38° (100°·4 F.), and has a density of

2·85 at 17° (62°·6 F.). It is readily soluble in ether, carbonic bisulphide, and the chloride and bromide of phosphorus. When slowly distilled, the orthosulphobromide appears to undergo decomposition, one of the compounds being a liquid of the composition P_2SBr_6, boiling at 205° (401° F.). At a low temperature this compound solidifies to a white mass which melts at −5° (23° F.). When treated with water it yields the hydrated phosphoric orthosulphobromide above mentioned. Another compound of the formula, PS_2Br, also appears to exist (Michaelis, *Ann. Chem. Pharm.*, 1872, clxiv. 9.)

CHAPTER XV.

HEXAD ELEMENTS.

(527) **Natural Relations of the Hexad Non-metallic Elements.**—Of this group the typical element sulphur has been already described; a marked analogy in chemical character is observable between it and selenium and tellurium. They are all characterized by a powerful attraction for oxygen. The properties of selenium are intermediate between those of sulphur and tellurium, which latter presents so much the external characters and appearance of a metal, that it is usually described with the metals. The specific gravity and fusing-point of these elements increase as the atomic weight increases, as will be seen by comparing the numbers in the different cases:

Elements.	Specific gravity.	Melting point.		Boiling point.		At wt.	Difference between at wts.
		°C.	°F.	°C.	°F.		
Sulphur ...	2·075	113	235·4	446	834·8	32	47·1
Selenium ...	4·788	217	422·6			79·1	49·9
Tellurium ...	6·33	482	899·6			129	

Amongst the compounds of each of these bodies with oxygen are two anhydrides; one with 2 atoms of oxygen corresponding with sulphurous anhydride, SO_2, and another with 3 atoms of oxygen corresponding with sulphuric anhydride, SO_3. One volume of the vapour of each of these three elements unites with 2 volumes of hydrogen to form 2 volumes of a sparingly soluble gaseous compound possessed of a very offensive odour and feebly acid character. Oxygen also presents a certain analogy with the members of this group, 1 volume of oxygen uniting with 2 volumes of hydrogen to form 2 volumes of steam; and the oxides and sulphides, generally, exhibit many points of resemblance. In general the members of this group exhibit dyad functions,

although in many cases they act as tetrads, sulphur forming a compound with four atoms of ethyl, $S(C_2H_5)_4$, and selenium and tellurium, each combining with 4 atoms of chlorine.

The atomic volume of solid sulphur is 15·6, and that of selenium 15·8, or nearly identical; but that of tellurium, 20·4, is one-fourth higher. It may be further remarked that the corresponding compounds of sulphur, selenium and tellurium are isomorphous.

The singular numerical relations which Dumas and others have pointed out between the atomic weights of the members composing these groups and those of several other elements equally closely allied, will be discussed hereafter.

It will be sufficient here to remark, that in groups of electro-negative elements of similar properties, it is observable that the element with the lowest atomic weight possesses the greatest chemical activity; sulphur, for example, being more active in its chemical relations than selenium, and selenium than tellurium: so, as we have already seen, fluorine is more energetic in its chemical actions than chlorine, chlorine than bromine, and bromine than iodine. In the metallic, or basylous elements, the order of their activity is exactly the reverse, potassium being more active than sodium and sodium than lithium.

The following table exhibits some of the corresponding compounds which the elements of this group form with oxygen and hydrogen:

H_2O Water.	H_2S Sulphuretted hydrogen.	H_2Se Seleniuretted hydrogen.	H_2Te Telluretted hydrogen.
	H_2SO_3 Sulphurous acid.	H_2SeO_3 Selenious acid.	H_2TeO_3 Tellurous acid.
	H_2SO_4 Sulphuric acid.	H_2SeO_4 Selenic acid.	H_2TeO_4 Telluric acid.

§ I. SELENIUM, Se=79·1.

Theoretic Density of Vapour, 5·4737; *Observed at* 1420° (2588° F.), 5·68; *Atomic Vol.* □; *Rel. wt.* 79·1; *Density Cryst.* 4·788; *Dyad as in* SeH_2; *Tetrad as in* $SeCl_4$; *Hexad as in* H_2SeO_4 [$SeO_2(OH)_2$]; *Mol. Vol. of Vapour* (SeSe)=□□; *Mol. wt.* =158·2.

(528) **SELENIUM** is a mythological name (from σελήνη, the moon), given by Berzelius to a rare elementary body discovered

by him during the year 1817, in the refuse of a sulphuric acid factory near Fahlun. It derives its chief interest from the remarkable analogy which it presents to sulphur. Selenium always occurs in combination; the compounds it forms with metals are termed *selenides*. The native selenides are very rare minerals, the most abundant of them being the selenides of iron, copper, and silver.

Extraction.—In order to obtain selenium in an isolated form, the Fahlun selenium residue is mixed with potassic nitrate and carbonate, and deflagrated; that is to say, the mixture is thrown in small quantities into a red-hot crucible, in which it burns vividly. The selenium and other bodies with which it is associated are oxidized at the expense of the oxygen of the nitre, whilst potassic selenate is produced by acting on the disengaged potash of the nitre. The mass is digested in water, acidulated with hydrochloric acid, and evaporated down to a small bulk; the selenic acid is thus reduced to selenious acid; $2HCl + H_2SeO_4 = H_2SeO_3 + Cl_2 + OH_2$: and the selenious acid, when treated with sulphurous acid, yields a precipitate of reduced selenium as a red, flocculent, amorphous powder; $2H_2SeO_3 + 4H_2SO_3 = Se_2 + 4H_2SO_4 + 2OH_2$.

Nilson (*Deut. chem. Ges. Ber.*, 1874, vii. 1719) treats washed Fahlun residues, which contain about 2·5 per cent. of selenium, with a moderately concentrated solution of potassic cyanide at 80°—100° (176°—212° F.) until the red colour of the powder becomes changed to grey. It is then thoroughly washed with boiling water, and the solution of potassic selenocyanate decomposed by hydrochloric acid, when the selenium is precipitated in red flocks. It still, however, contains some cupric and ferric selenide, from which it may be freed by converting it into selenious acid by treatment with nitric acid and subliming the anhydride; this is subsequently converted into the sodic salt, ignited to drive off any mercury that may be present, and reduced with sulphurous acid after the addition of hydrochloric acid, in the usual way.

Properties.—Selenium may be obtained in the amorphous, in the vitreous, and in the crystalline condition. When collected and dried, the pulverulent selenium begins to soften at a temperature below that of boiling water, and at a few degrees above 100° (212° F.) it melts; on cooling, it forms a brittle solid, with glassy fracture, metallic lustre, and deep brown colour, varying in density from 4·3 to 4·8. It has neither taste nor smell, is insoluble in water, and is a very bad conductor of heat and of

electricity. It is soluble in sulphuric acid, forming a green solution which deposits unaltered selenium when diluted; on heating the solution in concentrated acid, however, decomposition ensues and sulphurous anhydride is evolved. Selenium when melted is ductile, and may be drawn out into fine threads.

The statements regarding its point of fusion are discordant, owing to its power of existing, like sulphur, in several distinct modifications. If it be maintained for some hours at 93°·3 (200° F.)—*i.e.* below its melting-point—the temperature suddenly rises until it reaches 160° (320° F.), after which the selenium is found to have become granular and crystalline. The fusing-point of this variety is 217° (422°·6 F.) (Hittorf). Carbonic bisulphide, at its boiling-point, dissolves about 1 per cent. of vitreous selenium, and deposits it in minute rhomboidal prisms of density 4·5. If these crystals be heated to about 168° (334°·4 F.), they become almost black, and increase in density to 4·8, experiencing a molecular change, in consequence of which they are no longer soluble in carbonic bisulphide; when this black mass is melted and quickly cooled, it resumes its solubility in this menstruum, owing to its reconversion into the vitreous condition. Black selenium appears to be analogous to the rhombic form of sulphur, and the red amorphous variety, which has a density of 4·3, to that form of sulphur which is insoluble in carbonic bisulphide.

Willoughby Smith has recently discovered that the electric conductivity of the crystalline selenium undergoes a very remarkable change under the influence of light, and from the determinations of Sale (*Proc. Roy. Soc.*, 1873, xxi. 283), it appears that the resistance varies with the nature of the light to which it is exposed. A bar of selenium whose resistance in the dark was 330,000 ohms showed a resistance of only 277,000 in the orange of the solar spectrum, which decreased to 255,000 in the red, and to 220,000 just on the outside edge of the red, so that the effect is not produced by the actinic rays, but is at a maximum at a place nearly coincident with the locus of the maximum of the heat rays. The increase of conductivity is instantaneous, being nearly doubled when exposed to the full sunlight. The same effect is produced to a less extent by exposure to diffused daylight, or even to the light from a paraffin lamp or gas-burner. It has been conclusively shown that it is not due to the action of heat.

When heated in the air, selenium only ignites with difficulty, burning with a blue flame, a portion of it is at the same time volatilized in red fumes, emitting an odour resembling that of crude carbonic bisulphide; this is probably due to the formation of a protoxide of selenium, which, however, is not acid. If heated in closed vessels, selenium boils at a temperature below a red heat, and gives off a deep yellow vapour, which, according to Deville and Troost, is of density 7·67 at 860° (1580° F.); when heated to 1040° (1904° F.) this decreases to 6·37; whilst at 1420° (2588° F.) it is only 5·68 and has expanded, until, as in the case of sulphur, it occupies a bulk nearly equal to that of an equivalent of oxygen. The specific gravity of selenium vapour calculated on the supposition that it exactly corresponds with the volume of an atom of hydrogen is 5·4737. The vapour condenses in red flowers or in opaque metallic-looking drops.

(529) **SELENIURETTED HYDROGEN**; *Hydroselenic acid; Dihydric selenide;* $SeH_2 = 81{\cdot}1$; *Rel. wt.* 40·55; *Density, Theoretic,* 2·8061; *Observed,* 2·795; *Mol. Vol.* [ ].—This substance is a colourless inflammable gas, which resembles hydrosulphuric acid, but its odour is much more offensive. Berzelius found that a bubble of the gas no larger than a pea deprived him of the sense of smell for several hours. Seleniuretted hydrogen is produced when selenium and hydrogen are heated together, but the amount formed is a function of the temperature: it may be prepared by acting on selenide of potassium or iron, with dilute hydrochloric or sulphuric acid. This gas is soluble in water, and precipitates many metals from their salts in the form of selenides. Its solution has a feebly acid reaction; if exposed to the air it absorbs oxygen and deposits selenium. The selenides of the alkali-metals are soluble in water: those of cerium, zinc, and manganese, are flesh-coloured; most of the others are black.

(530) **CHLORIDES OF SELENIUM.**—Selenium unites directly with chlorine, forming two compounds, one a brownish volatile liquid, *selenium dichloride,* Se_2Cl_2, heavier than water, and slowly decomposed by it; the other a volatile, white, crystalline mass, *selenium tetrachloride,* $SeCl_4$, which is immediately decomposed by water into selenious and hydrochloric acids. A crystalline *iodide of selenium* has been obtained, and a bromide also appears to exist.

(531) **OXIDES OF SELENIUM.**—Selenium forms two compounds with oxygen, which yield acids when united with the elements of water; the first of these corresponds to sulphurous, and the second to sulphuric acid.

Selenious **Anhydride,** $SeO_2 = 111{\cdot}1$: *Rel. wt.* 55·55; *Theoretic Density of Vapour,* 3·8441; *Observed,* 4·03; *Mol. Vol.* [ ]. This compound may be obtained by burning selenium in a current of oxygen, but it is usually prepared by boiling selenium with nitric acid or aqua regia, by which the selenium is gradually oxidized and dissolved; the excess of nitric acid is then expelled by heat, leaving the selenious anhydride as a white infusible mass, which volatilizes at a temperature below redness, forming a yellow vapour, and condenses again in beautiful snow-white prismatic needles. The crystals are deliquescent, and their aqueous solution, which is strongly acid, possesses a sour burning taste. *Selenious acid,* H_2SeO_3 [$SeO(OH)_2$], in solution is speedily deoxidized by iron or by zinc, either of which, when digested in the liquid, throws down the selenium in the form of a reddish-brown powder. A solution of sulphurous acid also readily reduces selenium from the acid, and an alkaline solution of grape sugar exerts a similar action, but if an alkaline hydrate be used, the selenium formed dissolves; this is not the case, however, with the carbonated alkalies. As the selenious anhydride obtained on evaporating the nitric acid solution is apt to contain sulphuric acid, it is necessary to purify it; for this purpose it is dissolved in water, and baryta-water cautiously added until it no longer pro-

duces a permanent precipitate of baric sulphate. The solution is then filtered and evaporated, and the anhydride sublimed, when it is obtained quite free from sulphuric and selenic acids.

Selenites.—Most of the selenites, except those of the metals of the alkalies, are insoluble in water, but soluble in nitric acid. With the alkali-metals three classes of salts may be formed: normal selenites, with the general formula, M_2SeO_3, like disodic selenite, Na_2SeO_3 (a salt, $Na_2SeO_3.5OH_2$, containing 5 mols. of water has also been obtained): acid selenites, with the general formula $MHSeO_3$, like hydric sodic selenite, $NaHSeO_3.OH_2$; and hyperacid selenites, or quadriselenites, with the general formula MH_32SeO_3, like trihydric sodic selenite, $2(NaH_32SeO_3).OH_2$. The selenites are easily recognized by the peculiar odour of selenium which they emit when heated on charcoal in the reducing flame of a blowpipe; the selenites in solution, when treated with sulphurous acid, give a reddish-brown precipitate of reduced selenium.

(532) **SELENIC ACID**; *Dihydric selenate*; H_2SeO_4 $[SeO_2(OH)_2] = 145{\cdot}1$.—The anhydride of this acid is not known. The acid itself is most conveniently prepared by deflagrating selenium or any selenite with nitre, dissolving the residue in water, and precipitating it with a solution of plumbic nitrate; the insoluble plumbic selenate thus obtained is suspended in water and decomposed by a current of sulphuretted hydrogen, when plumbic sulphide is formed, and selenic acid is set at liberty: $PbSeO_4 + SH_2 = H_2SeO_4 + PbS$. The plumbic sulphide may be separated by filtration, and the solution of the acid concentrated by evaporation until it has a density of 2·609, when it contains 94·9 per cent. of selenic acid; but on exposing a hot solution over sulphuric acid in a vacuum, an acid of density 2·629, containing 97·4 per cent. of selenic acid, may be obtained. If heated beyond 290° (554° F.), it is decomposed into selenious anhydride, water, and oxygen. Selenic acid dissolves iron and zinc with evolution of hydrogen; it also attacks copper and even gold, if boiled with these metals, which are oxidized at the expense of the acid, selenious acid being disengaged; platinum is not attacked by it. Sulphurous acid is without effect upon selenic acid, but hydrochloric acid decomposes it by the aid of heat, chlorine and selenious acid being liberated; $H_2SeO_4 + 2HCl = H_2SeO_3 + OH_2 + Cl_2$. Selenic acid closely resembles sulphuric acid in its properties, and its salts are isomorphous with the sulphates.

Selenates.—Selenic acid is dibasic. Solutions of the selenates give white precipitates with salts of barium, strontium, and lead, owing to the formation of selenates of these metals. These precipitates are insoluble in dilute nitric acid. When the soluble selenates are boiled with hydrochloric acid, selenic acid is liberated, and is reduced to selenious acid: sulphurous acid will then precipitate reduced selenium from the solution. Baric selenate is similarly decomposed, and

may thus be distinguished from baric sulphate. When heated on charcoal in the reducing-flame of a blowpipe, the selenates emit the characteristic odour of selenium.

(533) **SELENIOUS DICHLORIDE,** or *Selenium Oxychloride,* $SeOCl_2 = 166{\cdot}1$.—When phosphoric pentachloride is added to selenious anhydride, great heat is evolved, and selenious dichloride and oxychloride of phosphorus are produced: $SeO_2 + PCl_5 = SeOCl_2 + POCl_3$. The dichloride is a colourless liquid which boils at 179°·5 (355°·1 F.), and has a density of 2·443 at 13° (55·4° F.). At 0° (32° F.) it solidifies to a colourless crystalline mass. Selenious dichloride, when boiled for some time with oxychloride of phosphorus, yields tetrachloride of selenium and phosphoric anhydride: $3SeOCl_2 + 2POCl_3 = 3SeCl_4 + P_2O_5$. On adding trichloride of phosphorus to selenious dichloride kept cool, tetrachloride of selenium crystallizes out, and the liquid turns red, dichloride of selenium being formed at the same time, thus: $3SeOCl_2 + 3PCl_3 = SeCl_4 + Se_2Cl_2 + 3POCl_3$.

(534) **SELENIOUS MONOCHLORIDE,** or *Selenious Chlorhydrate,* SeO_2HCl or $SeO(OH)Cl$, = 147·6.—Selenious anhydride rapidly absorbs dry hydrochloric acid with considerable rise of temperature, forming a yellow liquid, having the composition SeO_2HCl, which begins to decompose at 26° (78·8° F.), however. At a low temperature it takes up another molecule of hydrochloric acid, forming a yellow crystalline solid, $SeO_2.2HCl$. This decomposes readily, giving off hydrochloric acid and leaving SeO_2HCl. The corresponding bromine compound, $SeO_2.2HBr$, crystallizes in brilliant steel-grey plates, which are stable below 55° (131° F.), but at higher temperatures decompose into selenium, bromine, and water. Selenious monochloride and selenious anhydride mutually decompose one another, with liberation of finely divided selenium, which is readily soluble in carbonic bisulphide.

(535) **CARBON BISELENIDE;** *Carbonic Selenide;* CSe_2 is formed by the action of the moist vapour of carbon tetrachloride on phosphorus selenide: $CCl_4 + 2SeH_2 = CSe_2 + 4HCl$. It is a pungent liquid resembling the corresponding sulphur compound (Rathke, *Ann. Chem. Pharm.*, 1869, cliii. 199).

(536) **SULPHIDES OF SELENIUM.**—When sulphur and selenium are fused together in various proportions, the product does not crystallize on cooling, but on dissolving it in carbonic bisulphide and evaporating, crystals may be obtained. These, however, from Bettendorff and Rath's researches (*Pog. Ann.*, 1870, cxxxix. 329) do not appear to be definite compounds of sulphur and selenium. When, however, 4 mols. of sulphur and 2 of selenium are treated in this manner, large, orange-red, rhombic octohedra occur amongst the first crop of crystals, which approximately have the composition SeS_5. Ditté (*Compt. Rend.*, 1871, lxxiii. 625 and 660), by saturating a very dilute solution of selenious acid with sulphuretted hydrogen at 0° (32° F.), obtained a lemon-yellow powder consisting of a mixture of sulphur and sulphide of selenium, the reaction being $SeO_2 + 2SH_2 = SeS + S + 2OH_2$. This powder dried in a vacuum, moistened with carbonic bisulphide and allowed to stand, becomes crystalline, and the free sulphur may then be removed by treatment with a small quantity of carbonic bisulphide, and then with benzene. It forms small transparent, brilliant orange-yellow plates, of density 3·056 at 0° (32° F.). H. v. Gerichten (*Deut. chem. Ges. Ber.*, 1874, vii. 26) regards the yellow precipitate obtained on treatment of selenious acid with sulphuretted hydrogen as selenic disulphide, SeS_2.

Selenium, like sulphur, unites with sulphuric anhydride (429) forming a dark green compound, $SeSO_3$, insoluble in the anhydride. It dissolves in concentrated sulphuric acid with a green colour.

(537) **SELENIOSULPHURIC ACID,** $H_2SeSO_3 = 161{\cdot}1$, is said to be formed by the action of sulphurous acid solution on selenium, but it is scarcely known in the free state. Its potassic salt, however, may be obtained by digesting selenium with potassic sulphite; the solution after being diluted and filtered, is allowed to evaporate spontaneously, when *potassic seleniotrithionate*, $K_2SeS_2O_6$, crystallizes out in sparingly soluble slender lustrous prisms, followed by a crop of crystals of *potassic seleniosulphate*, which is the chief product of the reaction. Potassic seleniosulphate forms large thin hexagonal plates belonging to the rhombic system. It is very readily decomposed, acids throwing down the whole of the selenium in the free state. Baric salts give a precipitate of sulphite and free selenium.

Potassic seleniotrithionate may be prepared readily by mixing solutions of potassic thiosulphate containing excess of the neutral sulphite with a concentrated solution of selenious acid; the liquid becomes warm and the new potassic salt quickly begins to separate in slender needles, the quantity of which increases as it cools. The seleniotrithionate is somewhat more stable than the seleniosulphate, as acids do not precipitate selenium from its solutions in the cold, but only on boiling; moreover baric chloride gives no precipitate.

§ II. TELLURIUM: Te = 129.

Theoretic Density of Vapour, 8·9268; *Observed Density at* 1390° (2534° F.), 9·00; *Density of Solid,* 6·33; *Atomic Vol.* □; *Rel. wt.* 129; *Mol. Vol. of Vapour,* □; *Mol. wt.* Te_2, 258; *Dyad as in* TeH_2: *Tetrad, as in* $TeCl_4$: *Hexad as in* H_2TeO_4 [$TeO_2(OH)_2$].

(538) **TELLURIUM** is a rare substance discovered by Müller in 1782, but first investigated by Klaproth in 1798, and named by him from *tellus,* the earth. It is found chiefly in the mines of Hungary and Transylvania, and also in the Calaveras range, California, occasionally native and nearly pure, but generally combined with various metals, such as gold, silver, bismuth, copper, or lead, and has been observed by Harvey occurring along with arsenical iron pyrites in combination with arsenicum and sulphur; it is usually also accompanied by small quantities of arsenicum and selenium. Its most common ore is the black, foliated tellurium ore of Nagyag in Transylvania, which contains about 13 per cent. of tellurium in the form of tellurides of gold, lead, and silver, mixed with sulphides of antimony and lead, and some selenium. Some specimens, however, contain more than 90 per cent. of the element. It may be extracted from this mineral by first digesting the finely powdered ore in hydrochloric acid, to remove the sulphides of lead and antimony, and then after washing it, heating the residue with nitric acid; the solution of tellurous nitrate thus obtained is decanted, evaporated to dryness, and treated with hydrochloric acid, after which the

tellurium is thrown down as a brown powder by the addition of sodic sulphite to the acid liquid. It is better, however, after treatment with hydrochloric acid to boil the residue with nitro-hydrochloric acid until the insoluble portion becomes white; and then, after the gold has been precipitated from the clear solution by ferrous sulphate, or better with oxalic acid, the tellurium is thrown down by sulphurous anhydride: the first portions of the precipitate contain the greater part of the selenium present. For additional particulars regarding the extraction of tellurium, the reader is referred to *Gmelin's Handbook*, iv. 393; and papers by R. v. Schrötter in the *Chem. Centr.*, 1872, p. 434, and 1873, p. 370.

Properties.—Most English writers on chemistry class tellurium amongst the metals. It presents, however, a close analogy with sulphur and selenium, although it possesses a high metallic lustre, and resembles bismuth in colour. It is very brittle, fuses between 426° and 482° (800° and 900° F.), and at a high temperature is converted into a yellow vapour which, according to Deville and Troost, has a density of 9·00 at a temperature of 1390° (2534° F.). The distillation of tellurium is best conducted by heating it very strongly in a porcelain tube, and passing a current of dry hydrogen gas over it; the vapour of tellurium is thus mechanically carried forward, and condenses in drops and flexible crystalline needles in the cooler parts of the apparatus. According to Mitscherlich, tellurium, when solidified after fusion, exhibits a rhombohedral cleavage, a circumstance which seems to indicate its isomorphism with arsenicum and antimony. Tellurium is a bad conductor of heat and of electricity. When heated strongly in the air it takes fire, burns with a blue flame edged with green, and emits a peculiar characteristic odour, whilst thick white fumes of tellurous anhydride are produced. Like sulphur and selenium, tellurium is soluble in cold concentrated sulphuric acid, to which it gives a fine purple-red colour; on dilution it is precipitated unchanged: if, however, the solution in concentrated acid be heated, sulphurous anhydride is evolved and tellurous acid formed. Minute quantities of tellurium, when taken internally, impart a persistent and intolerable odour of garlic to the breath.

(539) **TELLURETTED HYDROGEN**: *Dihydric telluride*; $TeH_2 = 131$; *Density, Theoretic*, 4.5326; *Observed*, 4·489; *Mol. Vol.* [ ]; *Rel. wt.* 65·5.—The most interesting compound of tellurium is that which it forms with hydrogen. It is a gaseous body analogous to sulphuretted hydrogen, contains its own volume of hydrogen, and is possessed of feebly acid properties. It may be obtained by decomposing the alloy of tellurium with

zinc or tin, by means of hydrochloric acid. The gas which escapes burns with a blue flame; it reddens litmus, and has an odour which cannot be distinguished from that of sulphuretted hydrogen: with water it forms a colourless solution, which becomes brown by exposure to the air, owing to the oxidation of the hydrogen and separation of tellurium. Telluretted hydrogen precipitates most of the metals from their solutions, in the form of tellurides, which have a close analogy with the corresponding sulphides. The tellurides of the alkali-metals are soluble in water.

(540) Two *chlorides*, $TeCl_2$ and $TeCl_4$, have been obtained by the direct action of chlorine upon tellurium, both of which are volatile; the vapour of the dichloride is of a violet colour. They are decomposed by a large quantity of water. Corresponding *bromides* and *iodides* of tellurium have been obtained; they are all solid crystalline substances; the bromides sublime unchanged, but the iodides are decomposed by heat.

(541) **OXIDES OF TELLURIUM.**—Tellurium forms two oxides, TeO_2 and TeO_3, which correspond in composition to sulphurous and sulphuric anhydrides.

Tellurous Acid; $H_2TeO_3[TeO(OH)_2]=179$.—Tellurium is readily dissolved by nitric acid of density 1·25, and if the solution be poured into water, a white, bulky hydrate of tellurous acid is precipitated. It is slightly soluble in water, reddens litmus, and combines with the alkaline bases; these compounds are soluble. Tellurous acid has a bitter metallic taste: its anhydride may be obtained by gently heating the hydrate, or by boiling the nitric acid solution, when it is deposited in crystalline needles, which are only very slightly soluble in water. The anhydride ($TeO_2=161$; Density 5·93) fuses easily, forming a transparent glass, which is yellow whilst hot, but becomes white and crystalline on cooling. Tellurous anhydride possesses considerable volatility: if fused with potassic hydrate, potassic tellurite is formed.

Tellurites.—Three varieties of tellurites exist—namely, normal salts, M_2TeO_3; acid salts, $MHTeO_3$, and hyperacid salts, or quadritellurites, $MHTeO_3.H_2TeO_3$. The tellurites of the alkali-metals are soluble, those of the alkaline earths very sparingly so. The anhydride also, like many of the metallic anhydrides, combines with the stronger acids; the compounds which it thus furnishes have a metallic taste, and are said to act powerfully as emetics. Its salts with oxalic and tartaric acid are soluble. All the soluble salts in which tellurium acts as a basyl are decomposed if mixed with hydrochloric acid and heated with sulphurous acid; reduced tellurium is precipitated under these circumstances. With sulphuretted hydrogen, a black sulphide of tellurium is produced.

(542) **TELLURIC ACID**: $H_2TeO_4[TeO_2(OH)_2]=195$.—This is formed on gently heating tellurium or tellurous acid with nitre. A potassic tellurate is produced, which is converted into a

baric salt, and the barium is then separated by sulphuric acid. It is best, however, according to Becker (*Ann. Chem. Pharm.*, 1876, clxxx. 257), to oxidize the nitric acid solution of tellurous acid with plumbic peroxide, remove the lead from the filtrate with sulphuric acid, evaporate to dryness, wash with alcohol and ether, and finally to crystallize from a small quantity of hot water. Telluric acid crystallizes in striated hexagonal prisms, which have a nauseous metallic taste; they exert but a feeble action on litmus. These crystals are composed of $H_2TeO_4.2OH_2$. If heated nearly to redness they furnish telluric anhydride, and then assume an orange-yellow colour. This anhydride ($TeO_3=177$) is completely insoluble in water, and in nitric and hydrochloric acids, as well as in alkaline solutions.

Tellurates.—Telluric acid has but a feeble chemical attraction for bases, but, like selenic acid, it forms three classes of salts which may be represented by the general formulæ, M_2TeO_4; $MHTeO_4$; and $MHTeO_4.H_2TeO_4$. Their solutions, when acidulated, yield a black precipitate with sulphuretted hydrogen. When telluric acid, or one of its salts, is heated to redness, oxygen is disengaged and the telluric is converted into tellurous anhydride, or the tellurate into a tellurite of the basyl.

Tellurium, whether in the form of a soluble tellurite or in that of a tellurate, is thrown down from its solutions in the reduced form by zinc or iron; neutral solutions of the salts of both its acids are also reduced by ferrous sulphate and by stannous chloride; in these cases the tellurium falls in brown flocks. The tellurates of the alkali-metals when heated to redness in a tube with charcoal are reduced to tellurides, which dissolve in water, yielding red solutions.

(543) Tellurous oxide, like selenious oxide, absorbs hydrobromic acid readily: at 15° (59° F.) the compound $TeO_2.HBr$ or TeO(OH)Br, appears to be formed; *tellurous monobromide* crystallize in plates of a dark brown colour. At −14° (6°·8 F.) this substance absorbs 2 mols. more of hydrobromic acid, yielding almost black plates resembling iodine in appearance, and having a composition corresponding to the formula $TeO_2.3HBr$. When heated at 300° (572° F.) it loses water and hydrobromic acid, and leaves *tellurous dibromide* or *tellurous oxibromide*, $TeOBr_2$, of a pale yellow colour; at a still higher temperature it decomposes, tellurium tetrabromide, $TeBr_4$, volatilizing, whilst tellurous anhydride is left. Similar compounds, $TeO_2.3HCl$, and $TeO_2.2HCl$, are formed with hydrochloric acid; the last mentioned when heated behaves like the bromine compound, yielding *tellurous dichloride*, $TeOCl_2$, and ultimately the tetrachloride, $TeCl_4$ (Ditté, *Compt. Rend.*, 1876, lxxxiii. 336 and 446).

CHAPTER XVI.

B. SECOND DIVISION.—THE METALS.

§ I.—GENERAL PROPERTIES OF THE METALS.

(544) **General Characters of the Metals.**—The metals, as a class, are capable of receiving a high polish, and are then characterized by a peculiar brilliancy termed *metallic* lustre. They are exceedingly opaque to light, and are good conductors both of heat and electricity. Some of them are also endowed with ductility, or fitness for drawing into wire, and malleability, or extensibility under the hammer. Most of them have a high specific gravity. When separated from their compounds by electrolytic action, they appear at the platinode, or negative pole of the voltaic battery.

These properties are not developed equally in all the metals; in some metals one or more of them may be wanting altogether: and there are other substances, not metallic in their nature, in which some of these characters are strongly displayed.

(545) **Lustre, Opacity, and Colour.**—Although, when polished, all metals present the lustre termed metallic, yet most of them are devoid of it when in a minutely divided state. Iron, copper, platinum, gold, silver, and even mercury, may be readily obtained in this condition by processes to be mentioned hereafter.

If, however, these metallic powders be subjected to pressure under the burnisher, a sufficient approximation of their particles is produced to render them capable of reflecting light, and the metallic lustre reappears. This property admits of being applied in the fine arts; for instance, it is possible to make copies of medals or ancient coins, by employing finely-divided copper, which is introduced with the medal into a mould: by submitting it to pressure, an exact copy of the medal, with a beautifully polished surface, is obtained: the copy is then strongly heated, care being taken to exclude atmospheric air: during the ignition the copy shrinks a little in all directions, but a fac-simile is formed, which is extremely distinct: but it is reversed and a little smaller than the original.

Bodies which are not metallic occasionally assume a brilliant surface like the metals. Iodine, which in all its chemical relations is very far removed from the metals, yet possesses a brilliant

lustre; the same thing is observable in a form of carbon, termed by the workman *kish*, which escapes from the vent-holes of the moulds during the process of casting iron. The native form of carbon, known as graphite or plumbago, has received its popular name of *black-lead* from its metallic appearance.

Metals are among the most opaque bodies with which we are acquainted: but their opacity is not perfect. When reduced to exceedingly fine leaves, light is transmitted; for example, pure gold, of not more than $\frac{1}{200,000}$ inch, or $0^{mm}000125$ thick, allows a green light to pass.

The *colour* of the reflected light varies with the nature of the metal. In most cases it is nearly white, with a shade peculiar to each metal: the tints of silver, platinum, tin, cadmium, and palladium, are very similar; other metals, such as lead and zinc, have a bluish colour; others, like iron, calcium, and arsenicum, have a greyish hue; barium is pale yellow; strontium and gold are a bright yellow; whilst copper is of a red colour. By repeated reflections from the same metal a distinct colour is often rendered perceptible, although it is not seen upon looking at the polished surface. A red tint may thus be made evident in silver, and a violet tinge in steel.

Some of the metals possess a characteristic *odour;* iron, tin, and copper emit, on friction, a smell peculiar to themselves, and arsenicum, when volatilized, evolves a powerful odour of garlic. The taste of most of the soluble compounds of the metals is astringent or acrid, and of the peculiar kind termed metallic.

(546) **Hardness, Brittleness, and Tenacity.**—Great differences are observable between the *hardness* of the different metals; steel may be rendered hard enough to scratch glass, whilst lead will take impressions from the finger-nail, and potassium may be spread like butter. Many of the harder metals are very elastic and sonorous when struck; but these properties are more strikingly displayed in some of the alloys, or compounds of the metals with each other, as in the alloy of tin and copper used for bells, and in that combination of carbon with iron, known as steel, which, by its high elasticity, is pre-eminently qualified for the construction of the springs used in machinery.

The following table gives the scale of hardness of the principal metals, according to Bottone (*Pog. Ann.*, 1873, cl. 644), as estimated by observing the time required for a steel drill to penetrate to a determinate depth:

Metal.	Hardness.	Metal.	Hardness.
Manganese ...	1456	Gold ...	979
Cobalt ...	1450	Aluminium ...	821
Nickel ...	1410	Cadmium ...	760
Iron ...	1375	Magnesium ...	726
Copper ...	1360	Zinc ...	651
Palladium ...	1207	Lead ...	570
Platinum ...	1107	Thallium ...	565
Zinc ...	1077	Calcium ...	405
Silver ...	990	Sodium ...	400
Iridium ...	984	Potassium ...	230

The hardness of the diamond in the same scale was found to be 3010.

Closely connected with the hardness are the *brittleness* and the *tenacity* of metals, which are very variable. Some, like antimony, arsenicum, and bismuth, may be pulverized without difficulty in a mortar, whilst others, as iron, gold, silver, and copper, require great force to effect their disintegration. The brittleness of some of the metals is materially affected by temperature. Zinc, at the ordinary temperature, is so brittle that it cannot be bent at a sharp angle without danger of destroying its cohesion, whilst if heated to between 100° and 150° (or from about 212° to 302° F.) it may be wrought with facility; at 210° (410° F.) it again becomes so brittle that it may be easily reduced to powder in an ordinary mortar. Brass, an alloy of copper and zinc, on the contrary, becomes brittle at temperatures approaching to redness, but when cold it possesses considerable malleability.

Taking the tenacity of lead=1, the tenacity of the different metals, after annealing, will be represented according to Wertheim's experiment as follows:

Lead	1	Silver	8·9
Cadmium	1·2	Platinum	13
Tin	1·3	Palladium	15
Gold	5·6	Copper	17
Zinc	8	Iron	26

The tenacity of the metals has been measured by fixing firmly in a vice one end of a bar or wire of the metal, the strength of which is to be ascertained, and attaching to the other end a convenient support on which gradually increased weights are placed until the wire breaks. By comparing together the weights required to determine the rupture of the different metals for bars of equal section, a comparative table of tenacity may be formed. Various circumstances materially influence the strength of the same metal;* such as its purity, the mode in which

* Deville, for example, by melting cobalt in a crucible of lime, has obtained it free from carbon and other impurities, in the form of a ductile mass of such

the bar has been prepared (whether by casting, by forging, or by wire-drawing), the temperature at which the comparisons are made, the application or omission of the process of annealing, and the manner in which the tension has been exerted, whether gradually or suddenly. Different observers, in consequence of operating differently in some one or other of these respects, have obtained results which vary from each other considerably. The necessity of attention to these points will be evident on examining the results obtained by Wertheim (*Ann. Chim. Phys.*, 1844, [3], xii. 440), who has given an elaborate series of experiments upon the tenacity of different metals, the most important of which are embodied in the following table. The numbers represent the weight in kilograms which a bar of each metal of 1 square millimetre in section would support without breaking, both when the strain is gradually increased and when suddenly applied:

Metal employed.	15° (59° F.).		100° (212° F.).	200° (392° F.).
	Gradual.	Sudden.		
Cast steel, drawn		83·8		
„ annealed	65·7			
Piano wire (steel)	70·0	99·1		
„ annealed	40·0	53 9	59·10	50·90
Iron wire	61·10	65·1		
„ annealed	46·88	50·25	51·10	46·9
Copper wire	40·30	41·0		
„ annealed	30·54	31·68	22·10	
Platinum wire	34·10	35 0		
„ annealed	23·50	27·70	22·60	19·7
Palladium wire		27·2		
„ annealed	27·4			
Silver wire	29·0	29·6		
„ annealed	16·02	16·5	14·00	14·00
Zinc, commercial, drawn ...	12·80	15·77		
„ „ annealed ...		14·40	12·20	7·27
Pure zinc, cast	4·5			
Gold, drawn	27·0	28·4		
„ annealed	10·08	11·1	12·60	12·06
Cadmium, drawn	2·24			
„ annealed		4·81	2·60	
Lead, cast	1·25	2·21		
„ drawn	2·07	2·36		
„ annealed	1·80	2·04	0·54	
Tin, drawn	2·45	3·0		
„ „ annealed	1·70	3·62	0·85	

The numbers given by Baudrimont (*Ann. Chim. Phys.*, 1850, [3], xxx. 304) differ somewhat from these, as will be observed from the following table:

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tenacity as to furnish a wire capable of supporting twice as great a weight as a wire of pure iron of similar dimensions; and a wire of nickel prepared in a similar way, although inferior in tenacity to one of cobalt, surpassed one of iron in the ratio of 3 to 2.

Metals.	Temperature.		
	0° (32° F.).	100° (212° F.).	200° (392° F.).
Iron	205·4	191·7	210·3
Copper... ...	25·1	21 87	18·2
Platinum ...	22·6	19·28	17·27
Palladium ...	36·48	32·48	27 08
Silver	28·32	23·26	18·58
Gold	18·4	15·2	12·88

It will be seen, from an inspection of these tables, that the general effect of heat is to diminish the tenacity of the metals, except in the case of iron and steel, the tenacity of which seems to be somewhat increased by heating them to the temperature of boiling water; this is particularly so with iron: by a further elevation of temperature the tenacity is again diminished. The influence of annealing, or heating the bar to dull redness and allowing it to cool slowly, is still more remarkable, for by this means the tenacity of gold is reduced more than half, that of silver nearly as much, that of platinum about one-third, and that of iron and copper about a fourth.

According to Wertheim all circumstances which increase the density, as a rule increase the elasticity also. He finds the coefficient of elasticity of an alloy to be sensibly the mean of the coefficients of the metals which enter into its composition, even when the formation of the alloy is attended with change of volume. The passage of an electric current produces a momentary diminution in the elasticity, independently of the diminution caused by the rise of temperature which it occasions.

(547) **Malleability and Ductility.**—The following metals are termed malleable metals, *i.e.* metals which may be reduced to thin leaves either by lamination between rollers, or by hammering:

1. Gold
2. Silver
3. Copper
4. Platinum
5. Palladium
6. Iron
7. Aluminium
8. Tin
9. Zinc
10. Lead
11. Cadmium
12. Nickel
13. Cobalt.

Lithium, potassium, and sodium, as well as mercury when in a frozen state, and thallium, likewise admit of extension under the hammer. Gold far surpasses all the other metals in malleability, for it may be beaten out into leaves so thin that a square decimetre weighs less than 20 mgrms., or a square foot weighs less than 3 grains, and the film does not exceed the 280,000th of

an inch in thickness. Silver and copper may also be reduced to leaves of great tenuity. The other metals may be rolled into foil, but cannot be hammered into leaf. At the Industrial Exhibition of Breslau, 1852, an album of leaf iron was exhibited, the sheets of which did not exceed 0·01$^{mm.}$ in thickness, and a square decimetre of the leaf weighed only 776 mgrms. Quite recently Messrs. Hallam and Co. are said to have obtained leaves of iron of less than half this thickness: the sheets did not exceed $\frac{1}{4800}$ inch in thickness, or $\frac{1}{190}$ $^{mm.}$, and a square inch weighed only 0·36 grain. Nickel and cobalt are far less malleable than the other metals in the list. The metals become denser in rolling, and are often rendered so hard by the operation that they require to be annealed between every second or third rolling. During the processes of hammering and rolling, much heat is developed.

The metals may be arranged in the following order of ductility, the property being possessed to a nearly equal extent by the first five upon the list:

1. Gold	7. Cadmium	12. Tin
2. Silver	8. Cobalt	13. Lead
3. Platinum	9. Nickel	14. Thallium
4. Iron	10. Aluminium	15. Magnesium
5. Copper	11. Zinc	16. Lithium.
6. Palladium		

Ductility is peculiarly displayed by the first 7 metals on the list. Wollaston procured a wire of platinum, the diameter of which did not exceed the $\frac{1}{30,000}$ of an inch, or 0·00085 millim., by placing a wire of platinum in the axis of a small cylinder of silver and reducing the compound wire to the utmost practicable tenuity in the ordinary way, by drawing it through holes made in a hard steel plate, termed a draw-plate; the apertures through which the wire was made to pass diminishing in size by regular gradation. Both metals were thus attenuated, *pari passu*, and the silver was finally dissolved off by nitric acid, which left the platinum unacted upon. Gold wire equally fine was obtained by a similar process (*Phil. Trans.*, 1813). Steel wires of extreme fineness have been produced in a similar manner, the coating of silver, in this case, having been dissolved by the action of mercury. Zinc, tin, lead, magnesium, and even lithium, may also be obtained in the form of wire, but with difficulty, on account of their feeble tenacity. Matthiessen has succeeded in obtaining many of the softer metals such as sodium and lithium,

in the form of wire, by forcing them under strong pressure through an aperture in a steel die.

The malleability of a metal is not always proportional to its ductility; iron, although it may be reduced to wires of extreme tenuity, is not nearly so malleable as gold, silver, copper, and some other metals which are inferior to it in ductility. A few substances which are not metallic exhibit, when in a state of semifusion, a very perfect ductility. Half-melted glass shows this property in a marked degree; it may be spun into very fine threads, which have even been woven into a species of cloth, designed for ornamental purposes.

It is obvious that the properties of brittleness, tenacity, ductility, and malleability, must be materially dependent upon the texture of the metal. This is strikingly exemplified in the variation in tenacity exhibited by the same metal under different circumstances. Silver, in ordinary cases, is tough, ductile, and malleable; by repeated heatings and coolings, however, its particles arrange themselves in a crystalline manner, and it then becomes very brittle. Copper, when deposited in crystals by slow voltaic action, is very hard and brittle; but when the action is more rapid, it is soft and tough, and the metal then exhibits a fibrous character. It may indeed be stated, as a general principle, that the crystalline metals, such as zinc, antimony, bismuth, and arsenicum, are the most brittle; while those which, like iron, have a fibrous structure, are possessed of a high degree of tenacity.

The structure of a metal is easily displayed in many cases by placing it in solvents the operation of which is very gradual. Some of the metals which fuse readily may be obtained in crystals without difficulty, by allowing 2 or 3 kilos. of the melted metal to cool slowly, and pouring out the interior portions before the whole has had time to solidify; the walls of the cavity are then found to be lined with crystals on their inner surface. Bismuth is particularly well adapted for this experiment. The less fusible metals, such as copper, iron, and silver, are often deposited in the crystalline form from their solutions by slow voltaic action. Many of them—as, for example, gold, silver, and copper—occur native in crystals. A large proportion of the metals crystallize in forms belonging to the regular system.

(548) **Density or Specific Gravity.**—Wide differences are observable in the specific gravity of the metals. In the annexed table, variations are exhibited between the extremes of iridium and platinum, the heaviest known forms of matter, on the one hand, and lithium, on the other, which has little more than half

the density of water. The lighter metals are all characterized by their powerful attraction for oxygen; those which are least oxidizable possessing generally the highest specific gravity. In a few instances, the most marked of which is platinum, the density may be somewhat increased by rolling and hammering; but this is not usually the case.

Density of the Metals.

Metal.	Density.	Observer.
Platinum	21·53	Wollaston.
Osmium	21·4	Deville and Debray.
Iridium	21·15	Deville and Debray.
Gold	19·34	G. Rose.
Uranium	18·4	Péligot.
Tungsten	17·6	D'Elhuyart.
Mercury	13·596	Regnault.
Rhodium	12·1	Deville and Debray.
Thallium	11·91 to 11·81	Crookes.
Palladium	11·8	Wollaston.
Ruthenium	11·4	Deville and Debray.
Lead	11·36	Reich.
Silver	10·53	G. Rose.
Bismuth	9·799	Marchand and Scheerer.
Gobalt	8·95	Rammelsberg.
Copper	8·95 to 8·92	Marchand and Scheerer.
Nickel	8·82	Tupputi.
Molybdenum	8·62	Bucholz.
Cadmium	8·694 to 8·604	Stromeyer.
Manganese	8·013	John.
Iron	7·844	Broling.
Indium	7·362	Winkler.
Tin	7·292	Kupffer.
Zinc	7·146	Wertheim.
Chromium	6·81	Wöhler.
Antimony	6·71	Marchand and Scheerer.
Tellurium	6·25	Berzelius.
Arsenicum	5·959 to 5·7	Guibourt.
Barium	4·00	Clarke.
Aluminium	2·67 to 2·56	Deville.
Strontium	2·54	Bunsen.
Glucinum	2·1	Debray.
Magnesium	1·743	Bunsen.
Calcium	1·578	Bunsen.
Rubidium	1·52	Bunsen.
Sodium	0·972	Gay-Lussac and Thénard.
Potassium	0·865	Gay-Lussac and Thénard.
Lithium	0·593	Bunsen.

(549) **Fusibility.**—The melting-points of the different metals differ not less widely than their densities. Mercury, for instance,

remains fluid as low as $-38°{\cdot}8$ ($-37°{\cdot}9$ F.); potassium and sodium melt below the heat of boiling water. Tin, cadmium, bismuth, thallium, lead, and zinc melt below redness; antimony, calcium, and aluminium, above a red heat. Silver, copper, and gold require a bright cherry-red heat; iron, nickel, and cobalt a white heat; whilst platinum, iridium, rhodium, and several others, require the intense heat of the oxyhydrogen blowpipe, or even of the voltaic arc, to effect their fusion.

Order of Fusibility of the Metals.

Metal.	°C.	°F.	Observer.
Mercury	−38·8	−37·9	B. Stewart.
Rubidium	38·5	101·3	Bunsen.
Potassium	62·5	144·5	Bunsen.
Sodium	97·6	207·7	Regnault.
Lithium	180	356	Bunsen.
Tin	228	442	Crichton.
Cadmium	228	442	Stromeyer.
Bismuth	264	507	Rudberg.
Thallium	294	561	Crookes.
Lead	325	617	Rudberg.
Tellurium, Arsenicum	undetermined.		
Zinc	412	773	Daniell.
Antimony	about 621	1150	
Calcium, Aluminium	above a red heat.		
Silver	1023	1873	Daniell. 916° C. E. Becquerel.
Copper	1091	1996	
Gold	1102	2016	Daniell. 1037° C. E. Becquerel.
Cast iron	1530	2786	
Cobalt, Nickel, Wrought iron, Manganese	highest heat of forge.		
Molybdenum, Tungsten, Chromium, Palladium	agglomerate but do not fuse in the forge		1360°–1380° C. E. Becquerel.
Platinum, Rhodium, Iridium, Vanadium, Ruthenium, Osmium	require the heat of the oxyhydrogen blowpipe		1460°–1480° C. E. Becquerel.

Some metals near their melting-points, before undergoing complete fusion, pass through a soft intermediate stage, in which, if two clean surfaces be presented to each other, and strong pressure or hammering be employed, they unite, or weld together, so as to form one continuous mass. Iron, platinum, thallium,

lithium, and potassium afford the most striking instances of this. Palladium is also, in a minor degree, susceptible of it.

(550) Volatility.—Many of the metals admit of being volatilized without difficulty. Mercury, when heated under ordinary atmospheric pressure ($760^{mm.}$), boils, and is reduced to a colourless, transparent vapour, at $357^{\circ}{\cdot}25$ ($675^{\circ}{\cdot}05$ F.). It is important to observe that this vapour, although metallic, is not a conductor of electricity, and will allow the passage of electric sparks as readily as atmospheric air. The insulating power of mercurial vapour, on the one hand, and the small specific gravity of potassium, of sodium, and of lithium, on the other, show that there is nothing inconsistent with facts in the supposition that hydrogen itself, although gaseous, an insulator, and the lightest known form of matter, may possibly be a metal; in fact, it approximates very closely to this class of bodies in most of its chemical properties. On the other hand, if hydrogen and arsenicum are both metals, the compound formed by the union of the two should exhibit the properties of an alloy; this substance is, however, a gas at the ordinary temperature and condensable to a colourless transparent liquid exhibiting no metallic properties whatever. Eight of the metals are sufficiently volatile to be distilled from the compounds from which they are obtained, viz.:

Mercury	Zinc	Sodium
Arsenicum	Cadmium	Rubidium.
Magnesium	Potassium	

Arsenicum is volatilized below redness, and even before it has assumed the liquid form; cadmium requires a full red heat, 860° (1580° F.), and zinc a temperature of 1040° (1904° F.): whilst potassium, sodium, and rubidium require a still higher temperature. Those metals which are generally considered fixed in the fire are likewise volatilizable to a certain extent. In the process of lead smelting, one-seventh of the lead escapes up the chimney, and would be wasted unless means for collecting it were adopted. Even copper is not absolutely fixed in the fire. A remarkable illustration of this fact was shown to the late Professor Miller by his friend Dr. Percy: he had in his possession part of a beam which, for many years, was suspended over a furnace in a copper smelting house in Norway; the whole beam, of which this was a fragment, contained minute beads of metallic copper studded through its texture: the copper must have been raised in vapour and so deposited within its fibres. Gold has been found similarly studding the beams of refineries; and it

may be seen to undergo volatilization in the focus of an intensely powerful burning-glass. Platinum may be converted into vapour with scintillation in the oxyhydrogen jet, and silver has even been distilled in considerable quantities by Stas by the heat produced in the oxyhydrogen flame. Fine wires of the most refractory metals may be dispersed in vapour by passing the discharge of a powerful Leyden battery through them.

(551) **Conducting Power for Heat and Electricity.**—The great differences of expansion exhibited by different metals when exposed to equal increments of temperature, have already been pointed out (132); and it may be stated generally that each metal possesses a specific expansion; the conducting power of each metal, both for heat (149) and for electricity is also definite (276); in general it is found that the best conductors of heat are also the best conductors of electricity; but although conductors in the solid and liquid conditions, the metals are insulators in the aëriform state.

(552) **ALLOYS.**—Metals enter into combination with each other, and form compounds termed *alloys*, many of which are most extensively used in the arts. Comparatively few of the metals possess qualities rendering them suitable to be employed alone by the manufacturer; aluminium, zinc, iron, tin, copper, lead, mercury, silver, gold, and platinum, constitute the entire number so used. Arsenicum, antimony, and bismuth are too brittle to be used alone, but are employed for hardening other metals. Many of the physical properties of the metals are greatly altered by combination with others; the combination or alloy being often adapted to purposes for which either metal separately would be unfit.

Matthiessen has made a special study of the effects produced upon the physical properties of metals by alloying them with one another (*Jour. Chem. Soc.*, 1867, xx. 201). He concludes that the metals considered under this aspect may be divided into two principal classes; a small one, *A*, comprising lead, tin, zinc, and cadmium, which impart to their alloys their own physical properties in the proportion in which they themselves exist in the alloy; and a more numerous class, *B*, the members of which do not impart to their alloys their physical properties in the proportion in which they themselves exist in the alloy.*

* Probably brittle metals, like arsenic, antimony, and bismuth, should be excepted.

The alloys which Matthiessen has examined consist of two metals. These he divides into three groups;

1, Alloys formed by metals of the class A with each other;
2, Alloys of metals of class A with those of class B; and
3, Alloys of the metals of class B with each other.

Some of the physical properties of the metals are but little altered by alloying. The specific heat of the alloys and their expansion by heat are always the mean of that of their components; and they vary with the proportions of each component. The specific gravity of the alloys of metals of class A is also the mean of that of their constituents; but when metals of class A are alloyed with those of class B, the observed density is frequently a little above or below that which is given by calculation.

The fusing-point of an alloy is invariably below the mean of that of its components. In this respect, however, an alloy agrees with other mixtures; the chlorides when mixed with each other melt below the fusing-point of the mean, and often below the fusing-point of either constituent. The same thing is observed in mixtures of the carbonates with each other; it is also remarkably observed in the case of the silicates, as is well known both to the glass-maker and to the metallurgist: the latter avails himself of the fact to render his slags sufficiently fusible and liquid, by due admixture of various silicates.

A striking and well-known illustration of this increased fusibility of alloys is seen in what is known as *fusible metal*, an alloy of bismuth, lead, and tin. These metals, when melted together in the proportions of 4 parts of bismuth, 2 of lead, and 1 of tin, or nearly in the atomic proportion Bi_2PbSn, yield a mass fusible in boiling water, although the melting-point of tin, the most fusible of the three metals, is more than 110° (198° F.) higher, and that of lead is 220° (396° F.) higher; the easy fusibility of this alloy is always remarkable, even if the proportions of its constituents be considerably varied.

In the metals of class A, the conducting power for electricity is exactly proportional to the quantity of each metal employed, and the same thing is true as regards the conducting power of these alloys for heat; but when a metal of class B is alloyed either with one of its own class or with one of class A, a sudden decrease in conducting power both for electricity and for heat takes place.

Alterations in hardness and elasticity are still more easily perceived, and for many applications in the arts are of still

greater importance. When a metal of class B is alloyed with a small proportion of one of class A, its elasticity is much increased. Bars of copper, of tin, of zinc, or of lead, when suspended and struck, emit a dead sound; but when bars of a copper-tin alloy (bell-metal) or of copper and zinc (brass) are struck, they emit a clear ringing sound. On the other hand, bars of tin-copper with 12 per cent. of copper, or tin-lead with 20 per cent. of lead, emit very little sound when struck; showing no marked change when the metals of class A are alloyed together, or when alloyed with a small proportion only of a metal in class B. Similar results are observed when weights are suspended to spirals of hard-drawn wire: such spirals, if made of copper, silver, gold, or platinum, become nearly straightened when stretched by a moderate weight; but wires of equal dimension composed of copper-tin (12 per cent. tin), silver-platinum (30 per cent. platinum), and gold-copper (8·4 per cent. copper), scarcely undergo any permanent change in form when subjected to tension by the same weight. Many ductile metals belonging to class B are much increased in elasticity by being alloyed with each other.

Matthiessen gives the following approximative results upon the tenacity of certain metals and alloys for wires hard drawn through the same gauge (No. 23):

	lb.
Copper, breaking strain for double wire ...	25—30
Tin	under 7
Lead	„ 7
Tin-lead (20 per cent. lead)	„ 7
Tin-copper (12 per cent. copper)	about 7
Copper-tin (12 per cent. tin)	80—90
Gold	20—25
Gold-copper (8·4 per cent. copper)	70—75
Silver	45—50
Platinum	45—50
Silver-platinum (30 per cent. platinum) ...	75—80

Advantage is taken in the arts of this variation in the hardness and elasticity of metals produced by alloying them together.

Type-metal is a fusible alloy of tin, lead, and antimony, which expands at the moment of solidification so as to take the impression of the mould accurately, and is hard enough to resist wear without cutting the paper or being inconveniently brittle. The qualities of copper are also modified in an important manner by alloying it with other metals. Copper alone is not fit for castings, and it is too tough to be conveniently wrought in the lathe or by the file; but when alloyed with zinc it forms a much harder compound, which can be cast, rolled, or turned, and which

constitutes the different kinds of brass, the qualities of which can be varied by varying the proportions of the two metals. The addition of nickel to brass destroys its yellow colour, and produces the white compound metal known under the name of German silver. Copper and tin in various proportions yield the hard, tough, but moderately fusible compounds known as bronze and bell-metal.

When the metals combine with mercury, the resulting body is called an *amalgam*.

The ductility of metals is usually impaired by combination with one another. Alloys of two brittle metals are invariably brittle: such is the case with the compound of arsenicum and bismuth. Alloys of a brittle with a malleable metal are also brittle. Even when two malleable metals are united, the compound is sometimes brittle; gold, for example, when alloyed with a minute portion of lead, splits under the hammer. Generally speaking, the hardness of metals is increased by alloying them; of this a familiar instance is afforded by the standard coin of the realm: neither gold nor silver, when unalloyed, is sufficiently hard to resist attrition to the degree required for the currency, but the addition of one-tenth or one-twelfth of its weight of copper to either metal increases its hardness to the requisite extent.

In most cases these compounds of metals with each other are united by weak ties; for it appears to be necessary, in order to produce energetic union between any two bodies, that the substances when separate should exhibit great dissimilarity in properties. It has sometimes been questioned whether alloys are actually chemical compounds: definite compounds of the metals with each other, do, however, certainly exist, and some have been found combined in definite proportions in the native state. Such is the case with silver and mercury, which occur crystallized together in the proportion of an atom of each (AgHg). On forming alloys consisting of two metals only, it may be observed that if a solid metal be added to a melted metal, one of three different results may be obtained; either—1. The solid metal dissolves quickly with marked evolution of heat, as when gold is added to melted tin, or sodium to mercury: in these cases true chemical combination appears certainly to occur; 2. The solid metal dissolves quickly without any marked rise of temperature, as when lead is added to melted tin; or, 3. The metal dissolves slowly, as when copper is added to melted tin. In the last case the two metals separate partially on standing, so that it would appear that a perfect alloy is not formed, each metal being dissolved only to a limited

extent in the other, in the same manner as ether may to a certain extent be dissolved by water, and water to a certain extent by ether. Now, just as these two solutions may be mixed with each other, so may the alloys be mixed. Lead, for instance, will dissolve only 1·6 per cent. of zinc, and zinc 1·2 per cent. of lead. In like manner bismuth will dissolve 8·14 per cent. of zinc, and zinc 2·4 per cent. of bismuth.

Hence it appears that most alloys are either *mixtures* of definite compounds, with an excess of one or other metal, or *solutions* of the definite alloy in the excess of one of the metals employed, forming in their solid condition what Matthiessen calls a *solidified solution*. The separation of the components of alloys from each other is sometimes easily effected by simple means. For instance, by exposing brass to a high temperature, the zinc is volatilized, leaving the copper behind; and, from the alloy of arsenicum and platinum, a heat sufficiently long continued will expel almost the whole of the arsenicum. Even mere mechanical means will sometimes suffice to effect the separation. When silver, for example, is amalgamated with mercury, the amalgam formed is dissolved by an excess of mercury: this excess, however, may be almost entirely removed by squeezing the mass through chamois leather; the amalgam is retained in the solid form, while the superfluous mercury passes through the pores of the leather almost free from silver.

The chemical properties of an alloy are generally such as might have been anticipated from those of its components, but in many instances, the alloy of two oxidizable metals is much more readily oxidized than either of its constituents. An alloy of 1 part of lead and 3 parts of tin, for example, burns when heated to dull redness much more easily than its components, and becomes converted into a white ash, used in the preparation of enamels (638). Sometimes an alloy is completely soluble in an acid which is without action upon one of its components:—German silver, which is a combination of copper with zinc and nickel, is readily dissolved by dilute sulphuric acid, although the acid will not attack metallic copper; and in a similar manner, an alloy of platinum with ten or twelve times its weight of silver is entirely dissolved by nitric acid, although platinum itself completely resists its action.

The more important alloys will, however, be best considered separately when the individual metals which enter into their composition are described.

(553) **Condition in which the Metals occur in Nature.**—The ties which unite the components of an alloy are feeble, and are easily severed, but the compounds formed by the metal with the non-metallic elements, are for the most part held together by attractions of a very powerful order, and are much more interesting and important than the alloys, in a chemical point of view. Carbon and silicon combine in small proportion with some of the metals without appearing to destroy their metallic character, forming compounds which resemble the alloys more than any other class of combinations: the most remarkable instances of carbides and silicides are furnished by iron, which, in its modifications of steel and cast iron, is combined with variable quantities of these elements. Many of the compounds of the metals with sulphur have a metallic lustre, as galena and pyrites, yet they are destitute of the other physical properties by which metals are recognised: ductility, malleability, and power of conducting electricity are extremely impaired or altogether wanting. The metallic character is still more completely destroyed by oxygen, which converts the metals into bodies apparently earthy, as in the familiar cases of lime, magnesia, alumina, and zincic oxide; whilst chlorine and its allied group of elements form compounds which possess the qualities of true salts. The energy with which iron, zinc, and many other metals combine with oxygen is very remarkable; and the action of chlorine upon these metals at ordinary temperatures is even stronger.

The more common metals are very rarely met with in the uncombined form, although some of the less abundant are found naturally in the metallic condition, such as gold, silver, mercury, platinum, and copper. They are then said to occur in the *native state*. Many are found alloyed with each other; gold, for instance, forms native alloys with palladium and with silver, silver with mercury, and antimony with arsenicum. The occurrence of metals or natural alloys in nature is, however, an exceptional circumstance, the majority of the metals being in combination with other elements, such as oxygen and sulphur, which, from their powerful chemical attractions, and the abundance in which they occur, are the bodies most frequently associated with the metals; at other times arsenicum, and more rarely chlorine, are the mineralizing agents. These compounds, whether oxides, sulphides, arsenides, or chlorides, constitute what are termed the *ores* of the metals.

(554) **Distribution of the Metals.**—Next to silica in its various forms, the most abundant components of the rocks and

superficial portions of the globe, are the compounds of lime, alumina, and magnesia. These earths are oxides of metallic bodies, the attraction of which for oxygen is so intense that they are never met with native in the metallic state, although in their oxidized form they are everywhere scattered in abundance over the face of the globe. It is not so with those metals which man is in the habit of separating from their ores upon the large scale, and of employing in the metallic state for the various requirements of civilized society. Most of the ores of the highest importance and utility constitute but a comparatively small portion of the components of the earth's crust; but this deficiency in their relative proportion is more than compensated by the mode of their distribution, for they are not dispersed at random, or diffused in minute quantity uniformly throughout the mass of the earth, but are collected into thin seams or beds, which form *mineral veins*.

Man has hitherto penetrated but a very small depth into the body of the earth, the deepest excavation not being greater, in proportion to the diameter of the earth, than the thickness of an ordinary sheet of writing paper to a globe of two feet in diameter. Geological observations have shown, as may be distinctly seen in many railway cuttings, that a great part of the superficial portions of the globe consist of a succession of beds or layers—*strata*, as they are commonly termed—one above another: these beds occasionally retain their original horizontal direction; but usually they have been forced into an inclined position so as to form an angle with the surface. The same stratum is liable to great variations in thickness in different parts, but each bed is found to occur in a uniform position in the series, the successive strata following each other in regular order, the uppermost being those of most recent formation. In this way the London clay rests upon the chalk, the chalk upon what is termed the green-sand, the green-sand upon the gault, and so on. The stratified or *sedimentary rocks* rest upon others, which like granite, porphyry, and basalt, show no appearance of stratification, but bear marks, more or less evident, of having undergone igneous fusion.

Occasionally it happens that a thin bed of metallic ore forms a part of the regular succession of the strata: in Staffordshire, for instance, over many square miles of country, thin bands or seams of the ore termed clay iron-stone, varying in thickness from 5 to 20$^{cm.}$ (2 to 8 inches) are found lying between the beds of coal. Usually, however, the metalliferous masses occur in

still older formations; such as in the mountain limestone of Cumberland and Derbyshire, or in the granite and clay-slate, as in Cornwall: they are then found in fissures which traverse the ordinary strata of the district, and assume a direction which, although it never becomes quite vertical, still approaches it more or less. These fissures vary in thickness from a few centimetres to a metre or two: they are often filled with masses of basalt, granite, or trachyte (which have been injected from below, whilst the materials were in the molten state under the effects of subterranean heat), and then constitute what the miner terms *dykes;* but in other cases they are filled with metallic ores, and form mineral veins or *lodes*. The ore sometimes occurs nearly pure; at others mingled with quartz, fluor-spar, and various crystallized minerals, or else with earthy impurities of different descriptions. These veins extend from the surface downwards, often to a depth greater than can be followed even in the deepest mines. The veins which occur in the same district usually run in two directions, nearly at right angles to each other, the principal or original veins being traversed by the others. In Cornwall, for example, the metalliferous veins run nearly east and west, but they are occasionally intersected more or less obliquely by other lodes, to which the term of *caunter* (contrary) *lodes,* or *cross courses,* has been given.

These cross courses, however, are not always metalliferous; they often appear to have been occasioned by the action of a force emanating from below, which, after bending and splitting the original strata, produced the fissures which were subsequently filled with quartz, clay, and various minerals. Such cross courses as these frequently occasion the miner much trouble and perplexity, since the subterranean force necessary to produce them is often attended with great displacement of the original strata. A valuable vein of ore is from this cause frequently interrupted, and is sometimes lost altogether for want of knowing in what direction to seek for it. This sudden break in a vein and its displacement is, in mining language, termed a *fault*. It is very rare for a mineral vein to occur alone; usually several are found together.

The thickness of the same vein, as might be expected, is subject to great variations; at one time it dwindles to a mere thread, at others it attains a considerable size. The most productive veins usually occur near the junction of two dissimilar kinds of rock—the metallic ores having perhaps accumulated there in consequence of slow voltaic actions which have been going on

through countless ages, and which have been occasioned by differences in chemical composition of the two contiguous rocks: in Cornwall, for example, where so large a proportion of the mineral wealth of Great Britain is accumulated, the most important mines occur upon the junction of the granite with the clay-slate or *killas*.

(555) **Mining Operations.**—The existence of a vein having been ascertained, and its *dip** or inclination to the horizon, and general direction or *strike* having been determined, the miner commences by sinking a vertical pit or *shaft*, in such a manner that he calculates upon cutting through the lode at some 30 or 40 fathoms (from about 50 to 70 metres) below the surface. When he has reached the lode, he *drives* a gallery, or *level*, horizontally into it, right and left, raising the ore to the surface through the shaft. If the produce be such as to encourage him to proceed, a second shaft is sunk in the course of the lode, at the distance of about 100 yards or 90 metres from the first, and into this the gallery or level is driven, so as to facilitate the ventilation of the mine and the extraction of the ore. In order to be able to remove the ore from other parts of the lode above and below the point at which the first level is made, the shaft is continued downwards, and other galleries, or *cross cuts*, as they are termed, are made, both above and below the first level, at intervals of ten fathoms (about 18 metres), to meet the lode at different points; these cross cuts are at right angles to the levels.

Fig. 331 shows a vertical cross section of the lode at the Callington Mine. E S represents the engine shaft, V V the vein or lode, and *c*, *c*, the cross cuts. The levels cannot be shown in this view; but whenever a cross cut meets the lode, a level is driven east and west, in the direction of the lode itself.

Fig. 332 shows the arrangement of the levels in the same mine; E S represents the engine shaft, W, a second smaller shaft, and L, L, L, the different levels, the depths of which in fathoms are indicated by the numbers attached to them; these levels communicate at different points by short cuts, or *winzes*, as the Cornish miners term them; they are shown at *u*, *u*, in various parts, and are needed to facilitate the extraction of the ore from different parts of the lode. The different levels are not immediately over, or parallel to each other, but their direction and position varies with that of the inclination and direction of the lode. This is explained by fig. 333, in which the direction of these galleries is exhibited; it represents a *plan* of the mine, supposing the figures to refer to the levels shown in 332: the lode, it will be seen, does not preserve the same dip at all points, being much more nearly vertical at the right than at the left extremity of the plan. The cross cuts cannot be shown in fig. 332. The shaded

* The terms *dip* and *strike* have been illustrated by the roofs of a row of houses running east and west; the ridge pole shows the direction of the strike of the strata east and west, whilst the slope of the slates shows the dip to the north and to the south.

parts in this figure indicate the portions of the lode which have been already worked away. The galleries in the mine are supported by strong timbering, the object of which is to prevent the rubbish from falling in and overwhelming the men while engaged in their work.

FIG. 331. FIG. 332.

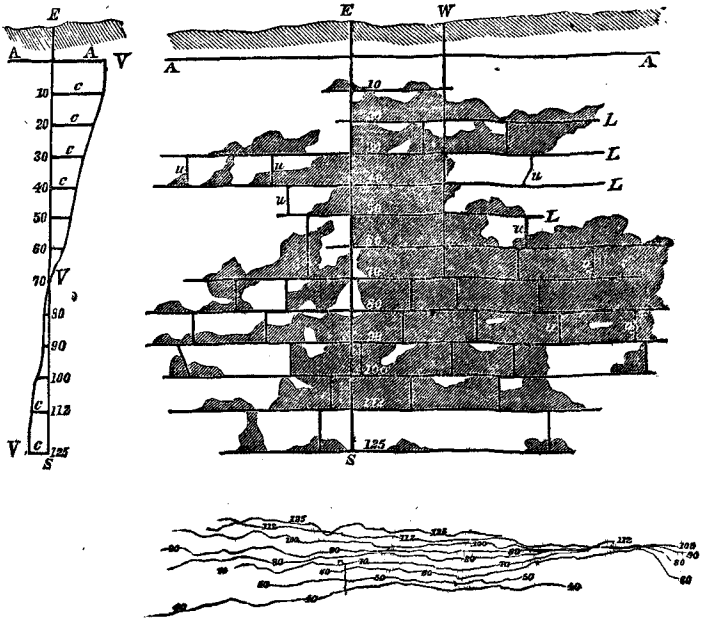


FIG. 333.

One of the principal difficulties which the miner has to contend with is the continual oozing of water into the mine in all directions. Where the mine, as very often happens, is situated upon the side of a hill, an *adit level*, or watercourse, shown at A, A, fig. 332, is carried from the shaft to the lowest accessible point of the surface, and through this the waters of the upper part of the mine readily escape; but when the workings extend below this point it becomes necessary to pump more or less constantly, and for this purpose powerful steam-engines are required. The galleries and levels are so constructed that the water shall flow from them into the principal shaft of the mine, so that by pumping from the *sump*, or lowest part of this shaft, the whole mine is freed from water. The greater part of the water is lifted only to the adit level, whilst the remainder is raised to the surface for the purpose of washing the ore.

Much of the excavation is done by hand, with the pickaxe and wedges; but after judicious clearing, gunpowder properly applied facilitates the progress greatly. The quantities of powder

used for blasting in the mines are small, usually about two ounces, or nearly 57 grams. The process of blasting consists in boring a hole to the depth of 18 inches or 2 feet (45 or 60 centimetres), somewhat obliquely, under the portion of rock which is to be raised; the powder is then introduced, and the hole is closed by ramming in clay or friable rock. A copper wire runs from the surface down to the charge, and when the ramming or *tamping* is finished, the wire is withdrawn, and its place supplied with a hollow rush charged with powder, and the train is fired by means of a fusee. A safety fusee is now commonly substituted for the copper wire and pithed reed filled with powder, and in hard rocks gun-cotton may advantageously be substituted for gunpowder. The ore that is detached is raised to the surface of the mine in large wrought-iron buckets, or *kibbles*, which are capable of containing about 3 cwt. of ore.

(556) **Mechanical Treatment of the Ores.**—The extraction of metals from their ores is effected by two classes of operations; those of the first class are mechanical; by their means the earthy parts contained in the matrix or vein-stone are to a certain extent separated: the operations of the second class are chemical, by which the metal itself is procured. The mechanical treatment is influenced not only by the nature and composition of the ore, but also by its market value: an ore of tin, of copper or of lead, from the higher price which the metal bears, will be worth a more elaborate treatment than an ore of iron or of zinc.

The ores of zinc and of iron are occasionally subjected to the operation of washing, for when they are accompanied by a loose friable clay, the clay admits of being readily diffused in a finely divided state through the water, and is easily removed by its means. The specific gravity of clay is not much more than 2·0, whilst that of ferrous carbonate and hydrated ferric oxide varies from 3·8 to 4·0, and that of calamine is about 4·2; consequently particles of these materials of equal size expose a smaller surface in proportion to their weight to the action of water than the clay, and when agitated with water they subside more rapidly; and if subjected to the action of a current of water, they are held for a shorter time in suspension, and are therefore carried by it to a smaller distance.

The same principles apply to the more elaborate processes of washing adopted with the ores of lead and tin. Galena has a specific gravity of 7·6; tinstone of about 7. Baric sulphate has a density of 4·6; fluor-spar of 3·1; and quartz of 2·65. When reduced to particles tolerably uniform in size, the earthy portions

may therefore be separated, to a considerable extent, from the ores of lead and tin by merely washing with water.

The following is an outline of the mechanical operations pursued in *dressing* the ores of lead and tin; and the same method is to a certain extent adopted with copper ores :—

The ore having been brought to the surface, if a lead or copper ore, is first sorted by hand: the purest portions or *prills*, as the Cornish miners term them, are set aside, and are ready for smelting without further preparation; but the bulk of the ore is broken by hammers into lumps of about the size of a walnut, and the best pieces are again picked out by hand. The rougher portions go to the crushing mill, which consists of a pair of horizontal cylinders placed parallel to each other at a little distance apart: the cylinders may be either grooved or plain. The ore is supplied to them by a hopper from above. After passing through the mill, the crushed ore is sifted through coarse sieves; the coarser parts are set aside for the stampers, and the finer portion is subjected to the operation of *jigging*. This consists in plunging the ore contained in a sieve into a pit, through which water is constantly flowing: the workman keeps the ore in continual agitation, alternately raising and lowering the sieve, to which he also gives an alternate rotatory motion, taking care always to keep it beneath the surface of the water. By this means, the contents of the sieve are separated into layers of different quality. If it be a lead ore which is undergoing treatment, the galena, from its friable character, is easily reduced to small fragments: most of the galena, therefore, passes through the sieve and subsides to the bottom of the pit, whilst what is left upon the sieve consists chiefly of the less friable fluor-spar and quartz. This residue is mixed with the inferior qualities of ore, and is transferred to the stamping mill, whilst the richer part is set aside for smelting.

Tin ore is usually disseminated through a compact hard matrix, and passes at once to the stampers.

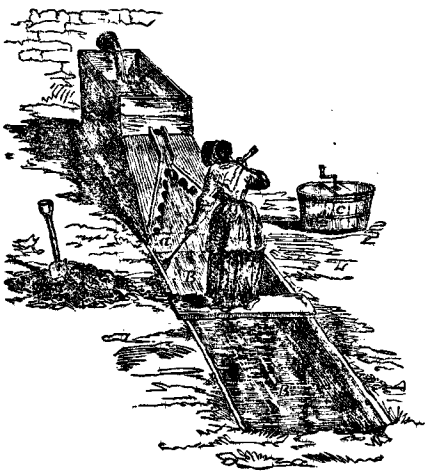
The stamping mill consists of five or six upright wooden beams, the lower ends of which are shod with iron, each beam weighing about $2\frac{1}{2}$ cwt. These are placed in a wooden frame, and are alternately lifted up and allowed to fall back upon the ore by the action of arms projecting from a horizontal axle, which is turned by water or steam power. The ore is placed on an inclined plane behind the stampers, so that it slides down under them, and is crushed. The crushed particles, when reduced to a sufficient degree of fineness, are washed out through a grating in front, by the action of a current of water which is constantly flowing

through the mill: the washed ore is carried into a channel in which two pits are formed; in the one nearest the mill the purer and heavier part of the ore, or *crop*, is deposited; whilst the more finely divided portion, technically termed *slime*, or *schlich*, accumulates in the second.

The crushed ore now undergoes a series of washings, the object of which is to separate the impurities from the valuable part of the ore.

The crop is first subjected to washing in the *buddle*; this is a wooden trough, fig. 334, nearly 2·5 metres long, 1 metre wide, and $0^{m}\cdot6$ deep, or about 8 feet long, 3 wide, and 2 deep, fixed in the ground, with one end somewhat elevated. At the upper end, a small stream of water enters, and is reduced to a uniform thin sheet by means of a distributing board, *a*, on which a number of small pieces of wood are fastened to break the stream. The ore to be washed is placed in small quantities at a time upon a board, B, somewhat more inclined than the body of the buddle, and it is spread out into a thin layer; the water carries it forward: the richer portions subside near the head of the trough, and the lighter ones are carried further down. "The heads" are then tossed in the *kieve*, or tub, shown at *c*, which is filled with water, and ore added by a workman, who keeps the contents of the kieve in continual agitation by turning the paddle or agitator, the handle of which is seen projecting at the top. When the vessel is nearly full, the agitation is stopped—the kieve is struck smartly upon the side several times; and its contents are allowed to subside; the upper half of the sediment is again passed through the buddle. Various modifications of the washing process are resorted to, but they are all the same in principle.

FIG. 334.



A rough estimate of the value of any sample of dressed ore is obtained by the process called *vanning*:—A small quantity of the ore is placed on a shovel, and agitated gently with a peculiar circular movement in water, then, by giving it a dexterous lateral shake, the different constituents arrange themselves according to their density—the galena, or the tinstone, at the bottom; above this are iron pyrites and blende; and at the top are the fluor-spar and quartz. The eye then at a glance roughly estimates the quantity of each.

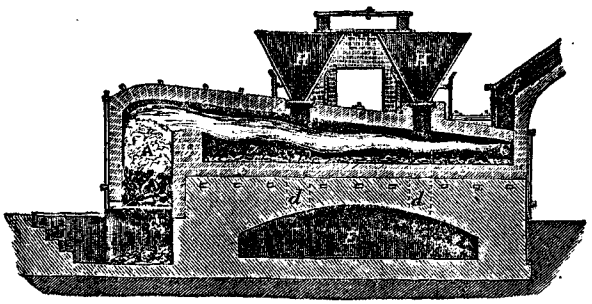
The water employed in the various washings is not allowed at

once to run to waste, but is made to pass through a long shallow channel, in which the slime and mud which have been carried away in the different operations may subside. This slime still retains some portion of ore; and in order to recover this as far as possible, it is again subjected to the action of a fine stream of water, either upon an inclined table, which acts in a manner similar to the buddle,—or it is washed upon a swinging table, the bed of which is also inclined, but moveable, and is suspended by chains from supports at the four corners; the bed is alternately thrust forward 2 or 3 inches (about 6 or 8 centimetres) by the revolution of a cam-wheel, and is then allowed to fall back against solid wooden bearings with a sudden jar. The ore is spread upon a board which overhangs the upper part of this table, and is carried forward by a gentle stream of water; the heavier particles of the ore, owing to the superior momentum which their density gives them, are by this jarring movement of the table carried back to the upper part of it, whilst the lighter impurities are washed away.

(557) **Roasting, *or* Oxidation.**—The chemical operations are divisible into two main branches, one dependent on the addition, the other on the removal of oxygen. If the mineral contain volatile ingredients, such as sulphur or arsenicum, the process of *roasting*, or oxidation, is first resorted to. In principle it is very simple; the mode of effecting it varies, however, in different cases. In the most common method, a furnace of particular construction, termed a *reverberatory*, is employed.

Fig. 335 shows a section of a reverberatory furnace, such as is employed for roasting copper ores; *t* is the platform, from which the hoppers, H, H, are charged with the ore, which at proper intervals is allowed to fall upon the bed,

FIG. 335.



e e: the fuel is consumed upon a distinct hearth, A, and does not come into contact with the ore, from which it is separated by the bridge, *b*: the heated gases, as they arise from the burning mass, are, from the construction of the arched roof, reverberated, or driven down upon the ore to be roasted, and then

pass off through the flue *f*: when sufficiently roasted, the ore is allowed to fall into the arched recess, E, beneath the bed of the furnace, through the openings, *d*, *d*, which are kept closed by sliding plates until the roasting is complete.

In roasting the ore in this furnace, care must be taken to prevent the heat from rising so high as to melt the mineral, which is stirred at intervals to expose fresh surfaces to the action of the current of heated air: the sulphur burns off in the shape of sulphurous anhydride, which is ordinarily allowed to escape into the atmosphere, whilst the arsenicum forms arsenious anhydride; most of the latter becomes condensed, and is collected on the sides of the chimney, or in chambers constructed for the purpose, whence it is removed at intervals, and subsequently purified. In metallurgic operations where sulphides of metals of different degrees of oxidability are present, it may happen that the sulphide of the more oxidizable metal is completely converted into a metallic oxide, with evolution of sulphurous anhydride, whilst the sulphide of the less oxidizable metal is reduced to the metallic state. For example, in roasting copper pyrites (the double sulphide of copper and iron), the iron is wholly converted into oxide, whilst the copper is extracted at once in the metallic state, by a series of careful roastings (1031 *et seq.*). In the case of plumbic sulphide, where the metal possesses but a moderate degree of oxidability, it is also the practice so to regulate the supply of air in the furnace that the sulphur is wholly expelled in the oxidized condition, whilst the greater part of the lead is extracted in the form of metal during a single roasting in the reverberatory (1056). Where the metal possesses a high degree of oxidability, as is the case with zinc, it is not practicable to limit the degree of oxidation in this manner during the roasting: the metal itself passes into the state of oxide, simultaneously with the elimination of the sulphur as sulphurous anhydride (777).

(558) **Reduction, *or* Smelting.**—The second chemical process for the extraction of the metals, that of *reduction*, is applicable to most metallic oxides, whether natural or artificial. The object in this case is to remove the oxygen, by heating the mineral with some substance which has a stronger attraction for oxygen than the metal itself possesses. The furnaces employed in this operation are often of great size, and vary in form with the nature of the metal: in them the ore is heated intensely in contact with carbon, which removes the oxygen as carbonic oxide and carbonic anhydride. It becomes necessary at this stage to get rid of the earthy and other impurities of the ore, which have not been completely removed owing to the imperfection of the mechanical

operations, and which often form a large proportion of the ore. In order to effect this, certain fluxes, or substances capable of forming fusible compounds with the earthy matters, are added at the same time as the carbon; these melt and form a kind of glass, through which the reduced metal, from its superior density, sinks, and is thus completely defended from contact with the air: the metal is drawn off at suitable intervals of time from the bottom of the furnace, whilst the melted glass—or *cinder*, as it is termed—runs off at an aperture left in the side for the purpose. Limestone is in some cases added to the ore with the view of aiding the fusion of siliceous impurities: in other instances fluor-spar or some other readily fusible material is added, for the purpose of increasing the fluidity of the slag. Much judgment is required in the selection of the flux, and in deciding upon the proper proportion to be added: frequently this object is economically effected by a judicious mixture of different ores of the same metal, each of which aids the other by supplying some compound which was wanted to render the slag sufficiently fusible.

The various modifications of these processes will be described in connexion with the different metals which require them. Other modes of separating individual metals are employed, which will be alluded to in their respective places. For details upon metallurgic processes, Percy's *Metallurgy*, or the fourth volume of Dumas' valuable work, *Traité de Chimie appliquée aux Arts*, may be consulted; and the second and third volumes of the same work contain many excellent descriptions of processes in which metallic chemistry is applied to the purposes of industry and commerce. Phillips's *Metallurgy* is a smaller and more compendious treatise on this subject.

(559) **Classification of the Metals.**—The metals may be divided into eight groups (page 13), regard being principally had in this arrangement to the convenience of indicating the method of testing for them, in the ordinary processes of analysis; it is often necessary on this account to depart from what may be considered as the natural order.

In treating of the groups of the non-metallic and electronegative elements, it has been remarked that the electronegative character of those belonging to the same group is most strongly marked in those which have the lowest combining number; chlorine, for example, being more active than bromine, and bromine than iodine. With the basylous or electropositive elements, the reverse generally holds good; the basic power of rubidium, for example, being greater than that of potassium, that

of potassium greater than that of sodium, and that of sodium being superior to the basic power of lithium.

I. The metals of the alkalies; these are five in number—viz.,

1. Potassium	3. Lithium	5. Cæsium.
2. Sodium	4. Rubidium	

The metals present a close analogy in properties; sodium, which is intermediate in properties between potassium and lithium, possesses a combining number which is the arithmetic mean of the two; for $\frac{39+7}{2}=23$. In like manner the atomic weight of rubidium (85·4) is intermediate between that of cæsium and potassium $\frac{133+39}{2}=86$. A similar remark is applicable to the intermediate members of some of the other groups.

The corresponding salts formed by the metals of the alkaline group are isomorphous only when they contain an equal number of molecules of water of crystallization. With these metals will be described the salts of ammonium; they present the closest analogy with the corresponding potassium compounds, and are isomorphous with them.

The metals of the alkalies are distinguished by the following characters:—They are monad or univalent, and therefore displace 1 atom of hydrogen from the acids. They are soft, easily fusible and volatile at high temperatures: they become tarnished immediately that they are exposed to the air, and possess such a powerful attraction for oxygen that they readily decompose water at the ordinary temperature with rapid disengagement of hydrogen: they each form at least two oxides, but only one of these, that with the smallest proportion of oxygen, forms salts: the general formula of this basic oxide is M'_2O. These basic oxides are acted on by water with great energy, yielding soluble hydrates of the general formula $M'HO$; their aqueous solutions are powerfully caustic and alkaline. When the oxides have once been converted into hydrates, the compounds thus obtained cannot be rendered anhydrous by heat alone. In these metals the basylous quality, or their capacity for saturating the acids, is developed to the highest degree. The hydrated alkalies, when exposed to the air, either in the solid form or in solution, absorb carbonic anhydride rapidly; each of the alkali-metals forms with carbonic acid two salts, a normal carbonate, and an acid carbonate commonly known as the bicarbonate, both of which are freely soluble in water. The metals of the alkalies combine with sulphur in several proportions; all of these compounds, also, are soluble. With chlorine they form but a single chloride. Lithium, from

the sparing solubility of its carbonate, furnishes the connecting link between this group and the one which follows it.

II. The metals of the alkaline earths are three in number—viz.,

1. Barium	2. Strontium	3. Calcium.

These metals are dyad, 1 atom usually displacing 2 atoms of hydrogen from its combinations, and as in the case of the metals in group I. the atomic weight of strontium (87·6) is intermediate between that of the other two metals of the group, $\frac{137+40}{2}=88{\cdot}5$. They decompose water at all temperatures with great rapidity; they each form two oxides which combine with water forming hydrates. The hydrates of the formula $M''H_2O_2$ are soluble to a certain extent in water, and are capable of forming salts by their action on acids; the hydrates, with the exception of that of barium, are decomposed by ignition. They each furnish but one chloride of the form $M''Cl_2$. The metals of this group are also powerfully basylous. They form several sulphides which are soluble in water, the protosulphides being less so than those which contain higher proportions of sulphur. Their carbonates are insoluble in pure water, but are soluble to a small extent in water charged with carbonic acid. They form insoluble phosphates and oxalates. The corresponding salts of these metals are in many cases isomorphous.

III. Metals of the earths: eight in number—viz.,

1. Aluminium	4. Yttrium	7. Lanthanum
2. Glucinum	5. Erbium	8. Didymium.
3. Gallium	6. Cerium	

The oxides of this class are insoluble in water; some of them are dissolved by solutions either of the caustic alkalies or of their carbonates. The phosphates of this group are insoluble in water. Aluminium and glucinum do not decompose water at ordinary temperatures unless the metals are in a very finely divided state: the other metals of this group are scarcely known in an isolated form, and their analogies are but ill-defined. The oxides of cerium, lanthanum, and didymium, are more or less coloured: those of the other metals are white. The basylous character of this group of metals is much less marked than that of the preceding ones. When salts of these metals in solution are mixed with ammonic hydric sulphide, precipitates consisting of hydrated oxides are formed, whilst sulphuretted hydrogen escapes. Many of these metals are very rare, and their properties have been but imperfectly examined. Aluminium, by the isomorphism of its oxide with ferric oxide, the volatility of its chloride, its slight

attraction for carbonic acid, and other peculiarities, connects this group with that of the iron metals.

IV. Magnesian metals, three in number:

1. Magnesium | 2. Zinc | 3. Cadmium.

Magnesium is sometimes reckoned as one of the metals of the alkaline earths; but from its power of resisting oxidation at the ordinary temperature of the air, its volatility at high temperatures, the isomorphism of its salts with those of zinc, the sparing solubility of its oxide and its sulphide, the solubility of its sulphate, and several other particulars, it stands in closer relation to zinc and cadmium. Magnesium, zinc, and cadmium are dyads; they all burn with flame when heated in air to a sufficiently high temperature, and each of these metals forms but a single oxide, chloride, and sulphide, as well as but a single class of salts with the radicles of the acids.

V. Metals more or less analogous to iron; six in number:

1. Cobalt	4. Iron
2. Nickel	5. Chromium
3. Uranium	6. Manganese.

They all act in combination as dyads in one series of their compounds, or as tetrad or pseudo-triad in another series, and some are hexad in a third: manganese appears to be heptad in permanganic acid, $HMnO_4$. These metals, when heated to dull redness in a current of aqueous vapour decompose it, and become converted into oxides, whilst hydrogen escapes: they also evolve hydrogen when dissolved in dilute sulphuric or in hydrochloric acid. The protoxides of the metals of this class are powerful bases: they have the general formula $M''O$. They yield hydrates, usually of the form $M''H_2O_2$, which part with their water readily when heated. These protoxides, with the exception of that of uranium, are dissolved more or less freely by ammonia, especially if ammonic chloride be present in the solution. Each of the metals of this group forms a sesquioxide, which, except in the case of cobalt and nickel, reacts with acids and forms corresponding salts: they also form oxides of the formula $MO.M_2O_3$ corresponding with the magnetic oxide of iron, $FeO.Fe_2O_3$. Several of the metals of this group—viz., iron, chromium, and manganese—form trioxides or even higher oxides, which are very soluble in water, and furnish powerful metallic acids. Hydrated sulphides of these metals are produced by the addition of a solution of sulphide of potassium or ammonium to a solution of their salts; the precipitate so occasioned is insoluble in excess of

the alkaline sulphide. The chromic salts, however, are precipitated as hydrated chromic sesquioxide, not as sesquisulphide. Sulphuretted hydrogen does not precipitate these metals from their solutions when acidulated with sulphuric acid. Corresponding salts furnished by the protoxides of this group are isomorphous, and the salts formed by the sesquioxides with the same acid are likewise isomorphous with each other. Chromium and manganese also exhibit an isomorphous relation to the sulphur group, inasmuch as the corresponding sulphates, chromates, and manganates have the same crystalline form. In the case of manganese a singular connexion with the halogens is exhibited in the isomorphism of the permanganates with the corresponding perchlorates and periodates.

VI. Metals which yield acids when their higher oxides are combined with water; of these there are twelve, as follows:

1. Tin	5. Molybdenum	9. Vanadium
2. Titanium	6. Tungsten	10. Arsenicum
3. Zirconium	7. Niobium	11. Antimony
4. Thorinum	8. Tantalum	12. Bismuth.

The first two of these metals are bivalent or dyads under certain circumstances, although usually tetrad or quadrivalent; the third and fourth are tetrads; the next two are sometimes tetrads, but often hexads, or equivalent to six atoms of hydrogen; the three which follow are pentad; whilst the last three, though usually triads, are occasionally, as in pentachloride of antimony, pentad or quinquivalent.

A close parallelism in properties exists between tin and titanium, corresponding compounds such as tinstone, SnO_2, and rutile, TiO_2, being isomorphous; each yields a liquid volatile tetrachloride, and in this particular, as well as in their powerful attraction for fluorine, they exhibit considerable analogy with silicon: zirconium is similarly related to silicon, furnishing a volatile tetrachloride and a dioxide; it also forms a series of compounds, the zircofluorides, containing fluorine, and analogous to the silicofluorides; whilst niobium, and tantalum, according to Marignac, and vanadium, according to the recent researches of Roscoe, all furnish an anhydride with 2 atoms of the metal and 5 atoms of oxygen, form a volatile pentachloride, and yield definite compounds with fluorine. Molybdenum and tungsten, have likewise strong analogies with each other.

Stannous oxide is a powerful base; but basic qualities are nearly wanting in the oxides of the other metals in this group.

The metals included in this group decompose water when its vapour is passed over them at a red heat (with the exception of arsenicum, which is more allied in character to phosphorus than to the metals): but they do not evolve hydrogen when treated with dilute sulphuric acid, owing to their want of basylous power. Many of them, owing to this tendency to form acids, decompose water with evolution of hydrogen in the presence of a powerful base, such as potassic hydrate. The metallic acids formed by these metals are, with the exception of arsenic acid, nearly insoluble in water. The persulphides of this group of metals are soluble in the sulphides of the alkali-metals, and in many cases form crystallizable compounds with them.

VII. The next group contains four metals :—viz.,

1. Copper	3. Thallium
2. Lead	4. Indium.

They are not related to each other by any strong chemical resemblances; copper and lead exert no decomposing action upon water, even at a full red heat; all form powerfully basic oxides. Copper and lead exhibit a considerable tendency to the formation of basic salts: they are not dissolved either by dilute sulphuric or by hydrochloric acid; they are precipitated from acid solutions by sulphuretted hydrogen, and their sulphides do not combine with the sulphides of the alkali-metals, but in the case of thallium the precipitation is incomplete. Copper forms salts which are isomorphous with those derived from the protoxides of the metals in the iron group, and in the compounds which it forms with carbonic acid, displays a close resemblance to magnesium and zinc, as well as to cobalt and nickel; and lead in some of its compounds is isomorphous with those of the alkaline earths, but in chemical properties it is more allied to mercury and silver; whilst in some organo-metallic compounds it has tetrad powers. Thallium and indium are both triad, but in many of its compounds thallium is a monad; copper is occasionally pseudo-monad, as in cuprous chloride, but in the majority of cases it is dyad in function like lead.

VIII. The last group consists of the noble metals, of which there are nine—viz.,

1. Mercury	4. Platinum	7. Ruthenium
2. Silver	5. Palladium	8. Osmium
3. Gold	6. Rhodium	9. Iridium.

These metals are unable to decompose water at any temperature. They have but a feeble attraction for oxygen, the oxides of the

first five being decomposed into oxygen and the metal by simply heating them to a temperature below visible redness, and in many cases simple exposure to a strong light produces a similar decomposition; all of them yield more than one series of salts. Mercury and silver are often found as minerals in the form of sulphides, but the other metals of this group usually occur in the native state, several of them being frequently associated together. Their attraction for sulphur and for chlorine is much stronger than for oxygen. All of them form two chlorides, and some three or even four: the chlorides of the noble metals have a strong tendency to form double chlorides with the chlorides of the metals of the alkalies.

Silver exhibits considerable analogy with lead: it is powerfully basylous; palladium is somewhat allied to copper.

§ II. General Properties of the Compounds of the Metals with the non-metallic Elements.

(560) **HYDRIDES.**—As far as is at present known, there are only five metals which form combinations with hydrogen:—viz., arsenicum, antimony, copper, sodium, and potassium. The first two of these compounds are gaseous, and are decomposed by a red heat into the metal and hydrogen. Many other metals, as iron, nickel, cobalt, manganese, platinum, and palladium, absorb hydrogen, some of them to a very large extent, but the hydrogen appears to be merely dissolved in the metal, at least in the case of the first four, whilst even in the case of palladium, which takes up several hundred times its volume of the gas, it is uncertain whether it forms a true compound. A few metals, such as zinc and potassium, appear under peculiar circumstances to undergo partial volatilization along with the hydrogen at the moment that this gas is evolved.

(561) **CHLORIDES.**—The simplest bodies produced by the combination of metals with the non-metallic elements are those obtained by the union of the metallic elements with the monad negative element chlorine. They may be considered as derived from one or more molecules of hydrochloric acid, in which the place of the hydrogen is supplied by a metal.

The principal groups of chlorides are the following:

1st. Chlorides of the type $'M'_2Cl_2 \left[\begin{matrix} MCl \\ MCl \end{matrix} Cl-M-M-Cl \right]$,

frequently called *Subchlorides*; as

Mercurous chloride (Calomel) . Hg_2Cl_2.

2nd. Chlorides of the type MCl, called *Monochlorides*; such as

Potassic chloride . . . . . KCl.

3rd. Chlorides of the type $M''Cl_2$, called *Dichlorides*; such as

Calcic chloride . . . . . $CaCl_2$.

4th. Chlorides of the type $M'''Cl_3$, called *Trichlorides*; such as

Antimonious chloride . . . . . $SbCl_3$.

5th. Chlorides of the type $'M'''_2Cl_6 \left[\begin{Bmatrix} MCl_3 \\ MCl_3 \end{Bmatrix} \right]$, frequently termed *Sesquichlorides*; such as

Ferric chloride . . . . . Fe_2Cl_6.

6th. Chlorides of the type $M^{iv}Cl_4$, called *Tetrachlorides*; such as

Platinic chloride . . . . . $PtCl_4$.

7th. Chlorides of the type M^vCl_5, called *Pentachlorides*; such as

Antimonic chloride . . . . . $SbCl_5$.

8th. Chlorides of the type $M^{vi}Cl_6$, called *Hexachlorides*; such as

Molybdic chloride . . . . . $MoCl_6$.

1. The chlorides $'M'_2Cl_2$, or *Subchlorides*, are few in number and of small importance, cuprous chloride and calomel, comprising all that are of interest; they are insoluble in water.

2. The chlorides MCl, *Monochlorides*, or *Protochlorides*, form an important group, including the chlorides of the alkali-metals, and those of silver and thallium, as well as aurous chloride. Aurous and argentic chlorides are insoluble in water; thallous chloride is but sparingly soluble. Aurous chloride is decomposed by a heat below redness, but the other chlorides fuse readily when heated, and may even be slowly volatilized without decomposition. They are conductors of the voltaic current when fused.

3. The chlorides $M''Cl_2$, or *Dichlorides*.—The compounds contained in this group are formed by the union of 1 atom of a metallic dyad with 2 atoms of chlorine. They present characters which are similar to those of the foregoing group, to which, indeed, they bear the closest resemblance: they were until quite recently considered to form part of it, having been usually described as protochlorides.

Amongst the members of this group are the chlorides of many highly basylous metals, such as barium and calcium. The chlorides of the less electropositive dyads, like that of mercury, differ greatly in properties from these basylous chlorides. All the chlorides of this group, when anhydrous, are solid at common temperatures; but when heated in vessels from which air is excluded, they may all be melted without undergoing decomposition, except those of copper, platinum, and palladium. Cupric chloride loses half its chlorine and becomes converted into cuprous chloride, whilst platinous chloride, $PtCl_2$, and palladious chloride are decomposed into free chlorine, and a residue of the pure metal. Several of the chlorides remain semi-transparent after fusion, and furnish soft and sectile masses, somewhat horny in aspect. Many of these chlorides, such as those of zinc and mercury, may be distilled without decomposition. Plumbic chloride is but sparingly soluble; platinous chloride, in one of its modifications, is quite insoluble; the other members of the group are freely soluble in water.

4. The next group, $M'''Cl_3$, comprises those known as *trichlorides* or *terchlorides*, of which the following are the most important:

Arsenious chloride	$AsCl_3$
Antimonious chloride	$SbCl_3$
Bismuth trichloride	$BiCl_3$
Thallic trichloride	$TlCl_3$
Auric chloride	$AuCl_3$.

Auric chloride is decomposed into aurous chloride by a moderate heat, and at a higher temperature loses all its chlorine; thallic chloride melts easily, and is decomposed at a high temperature, whilst the other three chlorides may be volatilized unchanged by a moderate elevation of temperature. They are decomposed by the addition of water: arsenious chloride into arsenious acid and hydrochloric acid, $AsCl_3 + 3OH_2 = 3HCl + H_3AsO_3$ [$\mathbf{AsCl_3 + 3OH_2 = 3HCl + As(OH)_3}$]; whilst the chlorides of antimony and bismuth furnish oxychlorides; $SbCl_3 + OH_2 = SbOCl + 2HCl$.

5. The chlorides, $'M'''_2Cl_6$, formerly called *Sesquichlorides*, constitute a remarkable group, of which the most important are aluminic chloride, ferric chloride, and chromic chloride. Each of these compounds contains 1 atom of the metallic element united with 3 atoms of chlorine, and is volatile at a high temperature without decomposition; the vapour density of the chlorides of aluminium and iron has been ascertained by experiment, and the result is remarkable, since if HH = 2 vols., Al_2Cl_6

is also = 2 vols. :* hence their formulæ should be doubled, as follows:

Aluminic chloride	Al_2Cl_6
Ferric chloride	Fe_2Cl_6
Chromic chloride (judging by analogy) ...	Cr_2Cl_6

The aqueous solutions of these chlorides undergo partial decomposition when evaporated, hydrochloric acid escapes, and a considerable portion of oxide of the metal is formed.

6. Next we have a group of chlorides, $M^{iv}Cl_4$, formerly described by chemists as the bichlorides, but now considered as *tetrachlorides*—viz.,

Titanic chloride	...	$TiCl_4$	Platinic chloride	...	$PtCl_4$
Stannic chloride	...	$SnCl_4$	Palladic chloride	...	$PdCl_4$
Zirconic chloride	...	$ZrCl_4$	Iridic chloride...	...	$IrCl_4$
Molybdic chloride	...	$MoCl_4$	Ruthenic chloride	...	$RuCl_4$
Tungstous chloride	...	WCl_4			

The first two compounds are liquid at ordinary temperatures, emit dense fumes when exposed to the air, and may be distilled unaltered. With the exception of the tetrachlorides of platinum, palladium, iridium, and ruthenium, which by a high temperature are decomposed into metal and free chlorine, the remaining compounds are fusible volatile solids, and may be sublimed unaltered in vessels from which air is excluded. The tetrachlorides of tin, titanium, and the noble metals, form crystallizable double salts with the chlorides of the alkali-metals.

7. The chlorides MCl_5 or *Pentachlorides* are represented by pentachloride of antimony, $SbCl_5$, and pentachloride of molybdenum, $MoCl_5$, which correspond with pentachloride of phosphorus. They are both volatile, and are decomposed by water, the antimony compound forming an oxychloride if the proportion of water is small, but yielding hydrated metantimonic acid, with separation of all its chlorine as hydrochloric acid, if the quantity of water be large.

8. Parallel in properties with these volatile pentachlorides are the chlorides of the type $M^{vi}Cl_6$, the *hexachlorides*, of which tungstic perchloride, WCl_6, is an example. It is volatile and is decomposed by water.

At ordinary temperatures the action of chlorine upon the metals is generally stronger than that of oxygen; but if a metallic chloride be heated in a current of oxygen or of atmo-

* It is not improbable, however, that if the vapour density of these compounds was taken at a much higher temperature, it would be found to correspond to that required by the formulæ $AlCl_3$ and $FeCl_3$.

spheric air, the chlorine is expelled, and an oxide of the metal is produced. The only instances in which this decomposition does not take place, occur in the case of the chlorides of the noble metals and of those belonging to the first and second groups.

In the case of the metals which have but slight attraction for oxygen, the chlorides generally correspond in number with the oxides, and are analogous to them in composition; two atoms of chlorine occupying the position of one atom of oxygen in the compound. For instance, the corresponding chlorides and oxides of iron, tin, and gold are the following:

$FeCl_2$; FeO	$SnCl_2$; SnO	$AuCl$; Au_2O
Fe_2Cl_6 ; Fe_2O_3	$SnCl_4$; SnO_2	$AuCl_3$; Au_2O_3.

Yet it is easy to prepare the oxides by heating the hydrates obtained from solutions of the chlorides by precipitation; for example, in the case of the compounds of iron, the following reactions may be observed:

$$FeCl_2 + 2KHO = 2KCl + FeH_2O_2.$$
$$Fe_2Cl_6 + 6KHO = 6KCl + Fe_2H_6O_6.$$
$$Fe_2Cl_6 + 3BaH_2O_2 = 3BaCl_2 + Fe_2H_6O_6.$$

When the metal exhibits a strong attraction for oxygen, and forms a powerful base, the number of oxides frequently exceeds that of the chlorides.

In many cases chlorine unites with the oxides or sulphides of the metals forming *oxychlorides* or *sulphochlorides*; the compound produced when the oxide is soluble in water is remarkable for its bleaching properties, and has been regarded by some chemists as a soluble oxychloride. Sometimes the chloride of a metal combines with its oxide and forms an insoluble oxychloride, as is the case with the oxychloride of mercury, $3HgO.HgCl_2$. It is a still more frequent occurrence that a chloride of one of the alkali-metals combines with a chloride of one of those metals which have a feebler attraction for oxygen, and the oxides of which partake rather of the character of acids than of bases. Thus we have a double chloride of platinum and potassium, $2KCl.PtCl_4$, and a double chloride of gold and sodium, $NaCl.AuCl_3.2OH_2$. Indeed, the higher chlorides of the noble metals generally form double salts of this nature; and the same thing holds true in very many cases with the corresponding bromides and iodides.

Preparation.—1. Many of the metallic chlorides may be formed by heating the metal in a current of dry chlorine: in this

way the perchlorides of antimony and iron are prepared. 2.—If the basic oxides be heated to redness in a current of dry chlorine, oxygen is expelled and a chloride of the metal remains; but this process is never adopted for preparing the chlorides. 3.—The sulphides are generally more readily decomposed by a current of gaseous chlorine than the oxides, owing to the strong attraction of chlorine for sulphur; both the sulphur and the metal combine with the gas producing chloride of sulphur and a metallic chloride. The process, however, is seldom employed except in the course of an analysis. 4.—In cases where the chloride is volatile, like that of aluminium, glucinum, or titanium, the oxide of the metal may be mixed with charcoal, and a current of dry chlorine passed over the mixture; the charcoal removes the oxygen in the form of carbonic oxide, and the chlorine, uniting with the metal, forms a chloride which volatilizes and becomes condensed in the cool part of the apparatus. 5.—In many cases the chloride may be obtained by passing dry hydrochloric acid gas over the oxide or the sulphide of the metal heated to low redness, the attraction of hydrogen for oxygen and for sulphur greatly facilitating the progress of the decomposition. 6.—An easier method, in cases where it is applicable, particularly when the hydrated chlorides are required, consists in dissolving the metal itself, its oxide, or its carbonate, in hydrochloric acid, and concentrating the solution by evaporation until it crystallizes. The chlorides of cobalt, nickel, and calcium may be thus obtained. This process, however, fails in many cases, if the attempt be made to render the chloride anhydrous, particularly in the class to which the earths belong; chlorides of magnesium and aluminium, for example, lose their chlorine as hydrochloric acid when their solutions are evaporated; $MgCl_2 + OH_2 = MgO + 2HCl$. 7.—In some cases chlorides of the metals, such as those of gold and platinum, are obtained by dissolving the metal in *aqua regia*, and decomposing any excess of nitric acid by evaporation to dryness with an excess of hydrochloric acid; a pure chloride of the metal may be obtained on re-dissolving the residue in water. 8.—Many of the chlorides of the less electropositive metals are decomposed when heated with the more basylous metals. Stannic chloride, $SnCl_4$, may thus be obtained by heating metallic tin with an excess of mercuric chloride; and the trichlorides of antimony and bismuth can be prepared in a similar manner. Sometimes this process is employed for the purpose of isolating those metals whose oxides resist decomposition by the usual means. In this way sodium is employed to decompose aluminic or mag-

nesic chloride for the purpose of procuring the aluminium or magnesium in an uncombined form; and in a similar manner potassium is employed to obtain uranium from uranous chloride. 9.—The insoluble chlorides, such as argentic, plumbic, and mercurous chloride, may be formed by the addition of hydrochloric acid, or a soluble chloride, to a solution of the salts of these metals.

Decompositions.—All the metallic chlorides, excepting those of the metals of the alkalies and earths, are reduced when heated in a current of hydrogen. In many cases the reduction is easily effected, and this process is occasionally resorted to as a means of procuring certain metals in a state of purity. Iron, for example, may be obtained in fine cubic crystals by reducing ferrous chloride in this manner. It is necessary, however, to maintain a current of hydrogen of sufficient rapidity to carry away the hydrochloric acid from the reduced metal, as otherwise the chloride would, in most cases, be reproduced by the decomposition of the acid. All the chlorides, except those of the alkali-metals, and of barium and mercury, are decomposed when heated in a current of steam, generally leaving corresponding oxides; chloride of bismuth, however, leaves an oxychloride (Kunheim). All the soluble chlorides, when heated with sulphuric acid and black oxide of manganese, evolve chlorine gas. Other particulars relating to the chlorides have been already mentioned (341, 344).

(562) **Estimation of Chlorine in Metallic Chlorides.**—Chlorine is almost always estimated in the form of argentic chloride, AgCl, 100 parts of which represent 24·74 of chlorine. The solution should be acidulated with nitric acid, and gently warmed before adding the argentic nitrate. If iodine or bromine be present, it will be precipitated with the chlorine, and must be determined separately, the corresponding weight of argentic iodide or bromide being deducted.

The composition of an insoluble chloride or of a basic chloride may be ascertained, except in the case of argentic chloride, by boiling a given weight of the compound with a pure solution of potassic hydrate, and then determining the quantity of chlorine in the alkaline solution by means of argentic nitrate: before adding the solution of silver, the alkaline liquid must be filtered from the undissolved metallic oxide, and acidulated with nitric acid.

(563) **BROMIDES.**—These closely resemble the chlorides in chemical characters (452, 454), and may be arranged in corresponding groups: the bromides of the metals of the alkalies and

alkaline earths may be prepared by digesting a solution of the alkali or of the earth with bromine in slight excess; a bromide and a bromate of the metal are thus formed, and by evaporation to dryness and gentle ignition of the residue, the bromate is decomposed, leaving a pure bromide: a small quantity of charcoal may be previously added, by which the decomposition of the bromate is more easily effected. The bromide is removed from the excess of charcoal by solution in water. The other bromides may be prepared by acting upon the metals with bromine, either in a dry state or in the presence of water. They are also easily formed by dissolving the oxides or the carbonates in hydrobromic acid. Argentic and mercurous bromides are insoluble, and plumbic bromide is but slightly soluble, so that they are obtained as precipitates on mixing a solution of the metallic salt with an alkaline bromide.

Bromine may be precipitated from its solutions, by argentic nitrate, which occasions a white precipitate of argentic bromide, and, in the absence of chlorine, it can be estimated by this means, 100 parts of the bromide corresponding to 42·55 of bromine. If chlorine be present, the precipitate will consist of a mixture of bromide and chloride of silver: it must be collected and weighed in the usual manner. An aliquot part is then transferred to a porcelain boat of known weight, and reduced to the metallic state by being heated in a current of hydrogen; from the loss of weight sustained the amount of silver in the whole of the mixed bromide and chloride may readily be calculated.

From the above data the relative proportions of the bromide and chloride of silver may be calculated thus:—let m be the weight of the mixed bromide and chloride, and let s be the weight of the reduced silver; then if x represent the proportion of chloride, and y that of bromide of silver, it will be found that

$$m = x + y, \qquad \text{and } s = \frac{108}{143{\cdot}5}x + \frac{108}{188}y;$$

consequently y, or the argentic bromide in the mixture, $= m - x$; and x, or the argentic chloride in the mixture, $= 5{\cdot}6134\, s - 3{\cdot}2247\, m$.

Instead of reducing the silver to the metallic state, a part of the mixed argentic compound of known weight may be heated in a current of dry chlorine, which displaces the bromine in the silver bromide and converts it into chloride. The loss of weight multiplied by 4·2203 gives the amount of argentic bromide. In all these operations, the weighings must be made with the

greatest care, but even then they do not give accurate results when the proportion of bromine is very small.

(564) **IODIDES.**—These (461) may be formed by processes analogous to those employed for the bromides: the insoluble iodides, such as those of mercury, silver, and lead, may be obtained from a solution of potassic iodide, by mixing it with a solution of the metallic salt.

The iodides exhibit a strong tendency to form double salts, the iodides of the strongly basylous metals combining readily to form crystallizable double iodides with those of the less electro-positive metals, such as those of silver, mercury, and lead. The iodides also form double compounds with the oxides and chlorides: for example, there are several compounds of the iodide with the oxide of lead; and a combination of stannic chloride with stannous iodide, $SnI_2.SnCl_4$, may be obtained in orange-coloured crystals (Kane).

The quantity of iodine in a solution which contains iodides, if no chlorides are present, may be estimated by the addition of argentic nitrate slightly acidulated with nitric acid: the resulting buff-coloured argentic iodide, when collected and dried, contains 54·04 per cent. of iodine. If chlorine or bromine be present, the iodine must be precipitated by means of palladious chloride; the precipitate must be allowed to subside during ten or twelve hours, and may then be collected on a filter and dried at a temperature not exceeding 70° (158° F.): this precipitate is insoluble in cold dilute nitric or hydrochloric acid, but soluble in ammonia. It contains 70·457 per cent. of iodine. Iodine may also be separated from bromine and chlorine, but less perfectly, by a mixture of ferrous sulphate and cupric sulphate (1043).

(565) **FLUORIDES.**—The general properties of these compounds have been already given (443). The fluorides are usually prepared by the direct action of hydrofluoric acid either upon the metal or more usually upon the oxide of the metal. Those which are insoluble may be procured by mixing a solution of the metallic salt with one of potassic or sodic fluoride; whilst those which are volatile may generally be prepared by heating the oxide of the metal with sulphuric acid and fluor-spar.

Estimation of Fluorine.—A simple method of detecting and of approximatively estimating fluorine, when present even in very small quantities, has been proposed by Dr. G. Wilson. The following is the process slightly modified:—the substance, if it does not already contain silica, is mixed with pounded glass, placed in a retort, and made into a thin cream with oil of vitriol; the

mixture is next heated, and distilled into a flask containing a solution of ammonia; the silicic fluoride comes over, and is immediately decomposed: on evaporating the liquid in the flask to dryness on a water-bath, the silica is rendered insoluble, and can be collected and weighed, whilst the ammonic fluoride may be dissolved out with a little water, and the fluorine in it estimated as calcic fluoride by precipitating with calcic chloride in excess, collecting, washing, and drying the precipitate, and then after igniting it strongly, treating it with acetic acid to remove any calcic carbonate that may be present, again washing, igniting, and weighing. The calcic fluoride thus obtained contains 48·72 per cent. of fluorine. The proportion of silica in the insoluble residue as compared with the fluorine, however, is not very uniform.

(566) **OXIDES.**—The most important compounds of the metals with the non-metallic bodies are those which they form with oxygen. Many of the most abundant and valuable metallic ores are oxides; such as specular and magnetic iron ores, the different forms of hæmatite, and tinstone, the ordinary ore of tin.

The metallic oxides may be subdivided according to their chemical functions into 3 classes:—viz., 1, basic oxides; 2, saline or indifferent oxides; and 3, metallic anhydrides, which when hydrated form the metallic acids.

The atomic proportions in which the constituents of the principal varieties of metallic oxides are united are exhibited in the following table:

1. *Suboxides,* $_{\prime\prime}M_2O$ [$'\mathbf{M}'_2O$],* of the type H_2O; feebly basic, such as

Cuprous oxide $_{\prime\prime}Cu_2O$ or [$'\mathbf{Cu}'_2O$].

2. *Monoxides,*† M'_2O [$\mathbf{O}M_2$] or $M''O$, of the type H_2O; strongly basic, such as

Argentic oxide, Ag'_2O or [$\mathbf{O}Ag_2$] | Lime, $Ca''O$.

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* When the atom of a dyad enters into combination with powers equivalent only to those of the atom of a monad, the fact may be indicated as in the text, by placing two dashes at the bottom and to the left of the symbol; or by placing one dash to the right of the symbol indicating that one attraction of each atom is satisfied by the oxygen, and one to the left showing that the two atoms of the metal are united together by one attraction of each, thus $\begin{array}{c} M - M. \\ \backslash \quad / \\ O \end{array}$

† These oxides may, in fact, be regarded as compounds formed upon the type of a single molecule of water, HHO, if each atom of hydrogen in the

3. *Sesquioxides*, M'''_2O_3 and $'M'''_2O_3$, of the type H_6O_3, the oxides of the triad metals and of the tetrad metals in the pseudo-triad condition; feebly basic, neutral or even acid, such as

Alumina, Al'''_2O_3 or $\left[{}'Al'''_2O_3 = \begin{Bmatrix} Al'''O \\ Al'''O \end{Bmatrix} O\right]$

Uranic sesquioxide, U_2O_3

Cobaltic sesquioxide, Co'''_2O_3 or $[{}'Co'''_2O_3]$

Arsenious sesquioxide, As'''_2O_3 or $\left[As'''_2O_3 = \begin{matrix} AsO \\ AsO \end{matrix} O\right]$.

4. Three-fourths oxides, M_3O_4, of the type H_8O_4: saline oxides, such as

Magnetic oxide of iron, $Fe''Fe'''_2O_4$, or $Fe''O.Fe'''_2O_3$

Chrome ironstone, $Fe''O.Cr'''_2O_3$.

5. *Dioxides*, $M^{iv}O_2$, of the type H_4O_2; rarely basic, but generally neutral or acid, such as

Platinic dioxide, $Pt^{iv}O_2$

Baric dioxide, BaO_2*

Stannic dioxide, $Sn^{iv}O_2$.

6. *Anhydrides*, $M^v_2O_5$, of the type $H_{10}O_5$

Arsenic anhydride, As_2O_5

Antimonic anhydride, Sb_2O_5.

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molecule is displaced by an atom of a metallic monad, such as potassium; or if both atoms of hydrogen be displaced by a single atom of a metallic dyad, such as barium, we have an analogous oxide; for example:

HHO, water,
KKO, anhydrous potash,
Ba″O, anhydrous baryta;

but if only one atom of hydrogen be displaced by the metallic monad we have a hydrate of the metallic oxide. If the metallic dyad displaces half the hydrogen of two molecules of water, we have a hydrate of the oxide of the metallic dyad, as for instance:

$\left.\begin{matrix} K \\ H \end{matrix}\right\}O$, potassic hydrate ; $\left.\begin{matrix} H \\ Ba'' \\ H \end{matrix}\right\}O$, baric hydrate.

In the sesquioxides and trioxides the *molecular* type is a group consisting of three molecules of water, each atom of the metal representing 3 or 6 atoms of hydrogen in the combination; alumina being $(Al''')_2O_3$, and its normal hydrate $Al_2H_6O_6$.

The dioxides correspond in composition to a group containing 2 molecules of water; the $\frac{3}{4}$ oxides to a group containing 4 molecules of water, and so on, as indicated in the table.

* Possibly $\begin{matrix} Ba \\ / \quad \backslash \\ O—O \end{matrix}$.

7. *Trioxides,* $M^{vi}O_3$, of the type H_6O_3; metallic anhydrides, such as

Molybdic trioxide,	$Mo^{vi}O_3$
Tungstic trioxide,	$W^{vi}O_3$.

8. *Tetroxides,* $M^{viii}O_4$, of the type H_8O_4

Ruthenic tetroxide,	RuO_4
Osmic tetroxide,	OsO_4

The oxides constitute so important a series of compounds, that it will be necessary to consider their relations, particularly to water and to the acids, somewhat more in detail, classifying them in the order just indicated.

1. *Suboxides,* of the type M_2O or $['M'_2O]$.—A few of the dyad metals, such as copper, lead, and mercury, form oxides in which one atom of the metal, which usually is equivalent to *two* atoms of hydrogen, becomes for the time equivalent only to a single atom of hydrogen. For example, we have cuprous oxide, or red oxide of copper, Cu_2O, and mercurous oxide, or black oxide of mercury, Hg_2O. Although these oxides usually give rise to an unstable series of salts, they frequently become decomposed into the normal oxide and free metal; cuprous oxide, for instance, being converted into metallic copper and the black oxide, $Cu_2O = Cu + CuO$; but with hydrochloric acid the reaction is as follows: $Cu_2O + 2HCl = OH_2 + Cu_2Cl_2$. No normal hydrates of these oxides appear to exist, the mercurous and plumbous oxide being anhydrous, and the yellow hydrated cuprous oxide being $4Cu_2O.OH_2$, instead of CuHO or $\left[\begin{Bmatrix}Cu(OH)\\Cu(OH)\end{Bmatrix}\right]$.

2. *Monoxides,* of the type M'_2O, or $M''O$.—This class of oxides includes all the most powerful bases: they are formed by the union either of 2 atoms of a metallic monad with 1 atom of oxygen, or by the union of 1 atom of a metallic dyad and 1 of oxygen. The first subdivision includes the five alkalies and the oxides of thallium and silver. Among the members of the second subdivision are included the alkaline earths, the oxides of lanthanum, didymium, thorinum, magnesium, zinc, and cadmium, and the protoxides of cerium, uranium, cobalt, nickel, iron, chromium, manganese, tin, copper, lead, mercury, and palladium. The anhydrous oxides of the alkali-metals become converted into hydrates with development of intense heat on the addition of water, which dissolves them rapidly and in large quantity; one molecule of water and one of alkali yielding two molecules

of the hydrate: *e.g.*, $KKO + HHO = 2KHO$. The hydrates of the alkalies cannot be again decomposed by exposure to heat, but are slowly volatilized without decomposition by a prolonged exposure to an elevated temperature. Hydrated argentic oxide is very unstable; it is only very slightly soluble.

The action of water upon anhydrous baryta, strontia, and lime is also very energetic, a single molecule of the hydrate being in each case formed by the combination of single molecules of water and the earth: as, for instance, $CaO + OH_2 = CaH_2O_2$. Calcic hydrate requires a full red heat for its decomposition, but the hydrates of baryta and strontia fuse at an elevated temperature, and baric hydrate does not part with water, even by prolonged ignition. These hydrates are soluble in water, although that of lime is but sparingly so. Magnesia combines very slowly with water. It is very sparingly soluble; plumbic and mercuric oxide are each somewhat more soluble. The other anhydrous oxides just mentioned do not combine with water when mixed with it. Their monohydrates can usually be obtained by precipitating a solution of one of their salts by the addition of a solution of one of the alkalies in slight excess. Hydrated cupric oxide has, however, the formula $CuO.2OH_2$, or CuH_4O_3; and the hydrated oxides of lead and tin consist of $2PbO.OH_2$, or $Pb_2H_2O_3$, and $2SnO.OH_2$, or $Sn_2H_2O_3$.

Most of the monoxides, by their reaction with the ordinary acids, form salts which are neutral in their action upon test-paper. The following equations may be taken as exemplifying some of the ordinary cases of the action of acids upon these oxides and their hydrates:

$$\begin{aligned} Ag_2O &+ 2HNO_3 = OH_2 + 2AgNO_3 \\ KHO &+ HCl = OH_2 + KCl \\ Tl_2O &+ 2HI = OH_2 + 2TlI \\ CaO &+ H_2SO_4 = OH_2 + CaSO_4. \end{aligned}$$

3. *Sesquioxides*, of the type M'''_2O_3 and $'M'''_2O_3$.—Most of the oxides of this class are feeble bases; among them are included alumina (probably also gallium), and the sesquioxides of cerium, uranium, iron, manganese, chromium, antimony, and bismuth. They furnish salts when acted upon by acids, but all these salts redden litmus: usually 3 molecules of water are separated by the reaction of the base upon the acid; as, for instance:

$$\begin{aligned} Cr_2O_3 &+ 6HCl = 3OH_2 + Cr_2Cl_6 \\ Fe_2O_3 &+ 3H_2SO_4 = 3OH_2 + Fe_23SO_4. \end{aligned}$$

These oxides of iron, antimony, and aluminium, however, occasionally, and uranic oxide invariably, form salts with the elimination of one molecule of water only, two-thirds of the oxygen remaining apparently in a state of intimate combination with the metal; for instance:

$$U_2O_3 + 2HCl = (U_2O_2)Cl_2 + OH_2.$$

Sesquioxides of cobalt and nickel exhibit no tendency to form salts by the action either of acids or of bases. When heated with hydrochloric acid, they evolve chlorine and furnish a lower chloride; no chloride corresponding to the sesquioxides being known:

$$Co_2O_3 + 6HCl = 2CoCl_2 + Cl_2 + 3OH_2.$$

Sesquioxide of arsenicum possesses no basic properties, being feebly but decidedly acid when dissolved in water; the sesquioxide of gold is insoluble in water, but its hydrate, $OH_2.Au_2O_3$, or $AuHO_2$, presents the properties of an acid, although they are only feebly marked.

The basic sesquioxides have but a feeble attraction for water; when precipitated by alkaline solutions from the solutions of their salts, they furnish very bulky gelatinous precipitates, which lose water during drying.

4. *Three-fourths Oxides*, of the type M_3O_4 or $M''O.M'''_2O_3$.—These oxides do not form salts with acids, being probably compounds of a protoxide with a sesquioxide; they are resolved into the corresponding compounds by the action of acids; as for instance: $Fe_3O_4 + 8HCl = FeCl_2 + Fe_2Cl_6 + 4OH_2$. Magnetic oxide of iron, Fe_3O_4 or $FeO.Fe_2O_3$, is the best representative of this class, which is rather numerous, and includes corresponding oxides of chromium, uranium, manganese, nickel, and cobalt, besides the double oxides, chrome ironstone, $FeO.Cr_2O_3$; spinelle, $MgO.Al_2O_3$; gahnite, $ZnO.Al_2O_3$.

5. *Dioxides* of the type M_2O_2 or $M^{iv}O_2$.

Of these there are three distinct varieties.

The first comprises the basic oxides, of which the platinic oxide, PtO_2, and palladic oxide, PdO_2, are the most important; they are feeble bases, and with water form hydrates, such as $PtO_2.2OH_2$ or PtH_4O_4.

The second variety is represented by the peroxides of sodium, Na_2O_2, and silver, Ag_2O_2, and those of barium, BaO_2, calcium, strontium, manganese, and lead. These oxides form either no corresponding salts or only very unstable ones: they retain the second atom of oxygen but feebly. When heated with sulphuric

acid they give off oxygen, and form a sulphate corresponding to the protoxide; $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + O_2 + 2OH_2$. When treated with hydrochloric acid they either furnish hydric peroxide, or liberate chlorine and form water; as for example:

1. $BaO_2 + 2HCl = BaCl_2 + H_2O_2$;
2. $PbO_2 + 4HCl = PbCl_2 + 2OH_2 + Cl_2$.

Of these dioxides some, as those of potassium and sodium, are decomposed with evolution of oxygen when thrown into water; baric dioxide forms the hydrate $BaO_2.6OH_2$, whilst the peroxides of manganese, lead, and silver do not become hydrated: the three oxides last mentioned conduct the voltaic current; plumbic dioxide, indeed, exhibits some properties of a metallic anhydride, and when fused with the hydrated alkalies furnishes compounds known as plumbates, whilst water is eliminated; $2KHO + PbO_2 = K_2PbO_3 + OH_2$.

In the third variety of dioxides the character of the metallic anhydrides is distinctly marked; such, for example, as the stannic and the titanic anhydrides, with which silica and zirconia ought also to be classed: these oxides do not unite directly with water, but yield hydrates possessed of feebly marked acid characters, when precipitated from their combinations. For each of these dioxides a corresponding chloride, containing 4 atoms of chlorine, may be obtained.

6. *Anhydrides*, of the type $M^v_2O_5$.

Arsenic, vanadic, and antimonic anhydrides, As_2O_5, V_2O_5, and Sb_2O_5 are the representatives of this group of oxides: when combined with water they furnish well-marked metallic acids. Arsenic anhydride is deliquescent and freely soluble; vanadic anhydride is slightly soluble; the antimonic compound does not combine with water when mixed with it.

7. *Trioxides*, of the type $M^{vi}O_3$.

This class includes the metallic anhydrides in which the acid property is most strongly developed; such, for example, as chromic, molybdic, tungstic, and ruthenic anhydrides. Although the ferric and manganic anhydrides have not been isolated, their place is obviously in this group. The molybdic, tungstic, and ruthenic anhydrides are insoluble in water.

8. *Tetroxides* of the type $M^{viii}O_4$.

There are two tetroxides belonging to this group, ruthenic tetroxide, RuO_4, and osmic tetroxide, OsO_4. They are both volatile, easily fusible, crystalline compounds which readily lose part of their oxygen.

The properties of the metallic acids or hydrated compounds obtained by the action of these dioxides, trioxides, and peroxides upon water, directly or indirectly, will be referred to hereafter, when the bodies themselves are described.

The compounds of the same metal with oxygen are often numerous; and the extremes, or the oxide with the maximum of oxygen, and the oxide with the minimum of oxygen, frequently present chemical qualities of opposite kinds, the former being electronegative, and possessing acid properties, whilst the lower oxides are electropositive, or basic in their nature.

An excellent example of this is afforded by the oxides of manganese: the protoxide, MnO, is a powerful base; the sesquioxide, Mn_2O_3, is a much weaker base; the red oxide, $MnO.Mn_2O_3$, is a saline or indifferent oxide, and shows little disposition to furnish corresponding salts by reaction with either acids or alkalies, and the same may be said of the black oxide, MnO_2; whilst the two higher oxides, when united with the elements of water form the manganic and permanganic acids, H_2MnO_4, and $H_2Mn_2O_8$. As a general rule, the greater the number of atoms of oxygen which an oxide contains, the less is it disposed to form salts by reaction with the acids; on the contrary, its hydrate frequently possesses acid properties, and then it reacts with bases to form salts.

The basic oxides in general are devoid of all metallic appearance, and present *par excellence* the characters of earthy matters. The protoxides, when solid, are all insulators of the voltaic current; but some of the higher oxides, such as the peroxides of silver, lead, and manganese, allow it to pass with facility. It is singular that all these conducting peroxides may be formed in solutions of salts of their respective metals by the action of the current itself.

The oxides when found crystallized in the native state, are much harder than the metals that furnish them, and generally have a specific gravity considerably less than that of the metals themselves. All the metallic oxides are solid at ordinary temperatures, although many of them are fusible at a red heat, such, for example, as the protoxides of potassium, sodium, and lead, and the sesquioxide of bismuth; cupric oxide, molybdic trioxide, chromic sesquioxide, and black oxide of iron, however, require a much higher temperature to effect their fusion. Baryta, strontia, and alumina require the heat of the oxyhydrogen jet; whilst some oxides, such as lime, yttria, and zirconia, exhibit no appear-

ance of fusion, even after the application of this intense heat.

As a general rule, the addition of oxygen to a metal renders it much less fusible and volatile. Ferrous oxide, chromic sesquioxide, and molybdic trioxide, are the only oxides which melt at a temperature below that of the metal from which they are produced. A few of the oxides are volatile at moderate temperatures; amongst these are arsenious and antimonious sesquioxide and osmic tetroxide. Nine only of the basic oxides are soluble in water to any considerable extent—viz., the five alkalies, and baryta, strontia, lime, and thallous oxide. The insolubility of the oxides, however, is in general far from being so complete as that of the corresponding sulphides, so that in analytical operations, except in particular cases, it is advisable to separate the metals in the form of sulphides; the oxides of lead, silver, and mercury in particular, are perceptibly soluble in pure water.

Those hydrated compounds of oxygen with the metals which possess acid characters—such as the chromic, manganic, and arsenic acids—are often freely soluble in water; but even those acids, which, like the tantalic, molybdic, and tungstic, are only very sparingly soluble, usually redden litmus-paper, although their anhydrides produce no such effect.

Preparation.—Most of the oxides may be obtained in combination with water, and are generally prepared by the decomposition of a solution of one of their salts by an alkaline hydrate: in this manner, zincic sulphate yields hydrated zincic oxide when its solution is precipitated with potassic hydrate; $ZnSO_4 + 2KHO = K_2SO_4 + ZnH_2O_2$. The metals which form powerful bases, like the alkalies and alkaline earths, retain the water with great obstinacy; whilst others, which are less powerful bases, such as hydrated cupric oxide, are decomposed at a temperature below that of boiling water.

The anhydrous oxides may be obtained in several ways: 1.—They may often be formed directly, by burning the metal in air, or in oxygen. This process is best adapted to metals which, like zinc or arsenicum, are volatile, or which produce fusible oxides, like iron or lead; in such cases the oxide is removed as fast as it is formed, and fresh surfaces of the metal are continually exposed to the action of the gas. Anhydrous potassic and sodic oxides are obtained by this method; and it is resorted to on the large scale in the preparation of arsenious anhydride, and of the oxides of zinc and lead. Several of the metallic protoxides, if roasted at a low red heat in a current of air or of

oxygen, absorb an additional quantity of oxygen. Litharge, or protoxide of lead, is thus converted into red lead, $2PbO.PbO_2$; and baric dioxide, BaO_2, may in this way be obtained from caustic baryta. 2.—Another method consists in the decomposition of a nitrate of the metal by means of heat, which expels the elements of nitric anhydride and leaves the oxide: in this way the oxides of mercury, bismuth, copper, barium, and strontium are prepared. 3.—In some cases it is found advantageous to prepare the oxide by the decomposition of the carbonate of the metal by heat. All the carbonates, with the exception of those of cæsium, rubidium, sodium, potassium, and barium, are decomposed at a red heat; lithic carbonate, however, is only partially decomposed: in this way lime is commonly prepared from limestone, which is an impure carbonate. 4.—Sometimes the hydrated oxide is first precipitated in the way already mentioned, and then rendered anhydrous by heat; this process is often employed for the preparation of ferric and uranic oxides. 5.—Occasionally the ignition of a sulphate is resorted to, as in preparing alumina and ferric oxide. 6.—All the acid oxides may be obtained by deflagrating the metal or its sulphide with nitre; the tendency of the metallic acid to form a salt by reaction with the alkali favours the oxidation of the metal: the higher oxides of osmium, titanium, manganese, and chromium, as well as of some other metals, may be obtained in this way. 7.—Some of the peroxides, as those of lead, manganese, bismuth, cobalt, and nickel, may be prepared by the electrolysis of their aqueous solutions, but a comparatively weak current should be used, otherwise a lower oxide is obtained.

Decompositions.—1. At a *red heat* many of the oxides lose their oxygen, either partially or entirely. The oxides of gold, silver, mercury, platinum, and palladium may thus be completely reduced; the peroxides of lead, cobalt, nickel, and barium, return to the state of protoxide; and the metallic anhydrides lose a portion of their oxygen; for example, arsenic and chromic anhydrides are thus converted respectively into arsenious anhydride and chromic oxide. The higher oxides of iron and manganese furnish the magnetic oxide, Fe_3O_4, and the red oxide, Mn_3O_4. It may be stated as a general rule, that the attraction of a metal for oxygen increases in the inverse proportion of its specific gravity; the lightest metals, such as potassium and sodium, being the most readily oxidized, whilst platinum, iridium, and gold, which are the densest metals, are also those which show the smallest tendency to combine with oxygen; this rule, however, is liable to exception, especially in the case of the acidifiable metals.

2.—The oxides are not affected by *hydrogen* gas at the ordinary temperature. All the higher oxides of the metals are reduced to protoxides by hydrogen at a low red heat, with simultaneous formation of water, whilst at a full red heat, a large number of them are reduced to the metallic state. This reduction goes on most readily when the current of hydrogen is brisk, so that the vapour of water is carried away as fast as it is formed. The oxides of many of the metals which decompose water at a red heat may nevertheless be deprived of their oxygen in a rapid current of hydrogen; this is the case, for example, with the oxides of iron, zinc, and cadmium, but not with those of chromium or manganese. The alkalies and the earths are not reducible by hydrogen.

3.—The reducing action of *carbon* at a high temperature is still more important; all the metals which yield their oxygen to hydrogen do so to carbon, moreover potassium and sodium are obtainable from their compounds by its agency. This arises in part from the volatility of these two metals, which is sufficient to enable them to be distilled from the carbonaceous mixture. Lithium and the metals of the earths are not sufficiently volatile to pass over in vapour, and although their attraction for oxygen is less intense than that of potassium or of sodium, they cannot be obtained from their oxides by the action of carbon. It depends upon the nature of the metal, and upon the temperature employed, whether the gas that is formed during the reduction be carbonic oxide or carbonic anhydride. The more readily oxidizable metals, such as potassium, zinc, and iron, decompose carbonic anhydride at a high temperature, so that carbonic oxide only is formed when they are reduced; whilst if the reduction takes place readily, as is the case with copper and lead, carbonic anhydride is obtained.

4.—Dry *chlorine* sometimes decomposes the basic metallic oxides, such as argentic and mercuric oxide, even without the application of heat, expelling their oxygen and converting them into chlorides. At an elevated temperature few of them, excepting magnesia, and the earths in the third group, resist its action: the oxides of gold and platinum are simply reduced to the metallic state, but chlorides of the metals are formed in other cases.

If the hydrated oxides be suspended in water, the action of chlorine is quite different; the metals of the first two groups yield bleaching compounds, and by heat are converted into chlorates and chlorides, in the manner already explained (358).

The oxides of the third group, the earths proper, experience no particular change, but those in the ferric group are converted into a mixture of chloride and hydrated sesquioxide. The sesquioxides of cobalt and nickel are usually prepared in this manner: for example, $3CoH_2O_2 + Cl_2 = CoCl_2 + Co_2H_6O_6$.

If the liquid be strongly alkaline, the whole of the metal may be converted into hydrated sesquioxide; $2CoH_2O_2 + 2KHO + Cl_2 = Co_2H_6O_6 + 2KCl$. The potassic hydrate in this case parts with its hydroxyl, which is transferred to the cobalt, whilst the chlorine combines with the potassium. The protoxide of manganese, under these circumstances, yields the hydrated peroxide, MnH_4O_4.

If the metal be capable of forming an acid with 3 atoms of oxygen, the process of oxidation may even proceed further, and the sesquioxide may, in the presence of a large quantity of potassic hydrate, become converted into the metallic acid, which reacts upon a portion of the excess of alkali and forms a salt, as in the case of ferric oxide, when potassic ferrate is produced; $Fe_2H_6O_6 + 10KHO + 3Cl_2 = 2K_2FeO_4 + 6KCl + 8OH_2$.

5.—Most of the oxides are decomposed more or less completely when heated with *sulphur*; the alkalies and alkaline earths are converted into a mixture of sulphate and sulphide, but magnesia, chromic oxide, stannic, and titanic anhydrides, as well as the earths proper, are unaltered. Most of the other oxides are converted into sulphides, with escape of sulphurous anhydride. The oxides are more readily decomposed by sulphur if they be previously mixed with carbon.

(567) **Estimation of Oxygen in Metallic Oxides.**—If the metallic oxide is capable of being decomposed by hydrogen its composition may be ascertained, by heating it in a current of the gas, and either collecting and weighing the water produced, or determining the amount of reduced metal which a given weight of the oxide has yielded. In other cases the composition of the oxide is determined synthetically, a given weight of the metal being converted into oxide, either by heating the metal in a current of air, or by converting it into a nitrate, and afterwards expelling the elements of nitric anhydride by the application of heat, and weighing the quantity of oxide which is left.

(568) **SULPHIDES.**—The combinations of sulphur with the metals are numerous, and in many instances are of great value, forming important ores. A large number of the native sulphides exhibit a high metallic lustre, as is the case with the sulphides of iron, copper, lead, and antimony.

Sulphur, like oxygen, frequently combines with the same metal in several proportions, and it usually happens that for each oxide a corresponding sulphide may be formed; the sulphides, indeed, present a close analogy with the oxides. Sometimes, as in the case of the metals of the alkalies and alkaline earths, the sulphides are more numerous than the oxides: for instance, three oxides of potassium and sodium, and two only of barium are known, but there are not fewer than five sulphides of each of these metals.

All the metallic sulphides are solid at ordinary temperatures. Most of them may be fused at a heat a little above redness, and if the air be excluded, the protosulphides undergo no change in composition; but many of the higher sulphides, such as ferric sulphide and stannic sulphide, SnS_2, are decomposed, and give off the second atom of sulphur, whilst a lower sulphide of the metal is left. Arsenious sulphide, or orpiment, As_2S_3, and mercuric sulphide, or cinnabar, HgS, may be sublimed if excluded from the air; that is to say, they may be converted into vapour, and recondensed in the solid form; indeed, these sulphides are usually purified by this operation.

The sulphides of all the metals are insoluble in water, with the exception of those of the alkali-metals and of strontium and barium; calcic and magnesic sulphides, moreover, are sparingly soluble.

If solutions of the sulphides of the metals of the alkalies and alkaline earths be subjected to a current of sulphuretted hydrogen, they combine with it, and form soluble compounds corresponding to the hydrates:

$$K_2S + SH_2 = 2KHS; \quad CaS + SH_2 = CaH_2S_2.$$

These have been termed *sulph-hydrates, thio-hydrates, hydro-sulphides,* or *hydric sulphides.* Those of calcium and magnesium are decomposed into hydrates by boiling with water:

$$MgH_2S_2 + 2OH_2 = MgH_2O_2 + 2SH_2.$$
$$[Mg(SH)_2 + 2OH_2 = Mg(OH)_2 + 2SH_2.]$$

Several of the thiohydrates may be obtained in crystals, if the solutions be evaporated out of contact with the air.

The sulphides, like the oxides, may be subdivided into basic and acid sulphides, according to the nature of the metal and the number of atoms of sulphur with which each atom of metal is combined. These may be supposed to be formed on the type of one or more molecules of sulphuretted hydrogen, as the oxides are upon the type of one or more molecules of water. The proto-

sulphides of the alkali-metals afford illustrations of basic sulphides, and they enter into combination with the higher sulphides of metals which, like antimony and arsenicum, form acids with oxygen. Arsenic sulphide, As_2S_5, in this way combines with disodic sulphide, and forms a soluble crystalline compound, $3Na_2S.As_2S_5.15OH_2$; in like manner antimonic sulphide, Sb_2S_5, forms a compound with disodic sulphide, $3Na_2S.Sb_2S_5.18OH_2$, or $Na_3SbS_4.9OH_2$, or $[\mathbf{Sb}S(SNa)_3.9\mathbf{O}H_2]$, which crystallizes in beautiful transparent tetrahedra. A large number of similar compounds may be formed with the sulphides of other metals, and these compounds are for the most part soluble in water; some of them, however, are not, as the potassic zincic sulphide, $K_2S.3ZnS$, obtained by fusing zincic sulphide with potassic carbonate and sulphur.

In consequence of the tendency to the formation of these double sulphur salts, many of the sulphides which are insoluble in water are dissolved freely by solutions of sulphide of potassium or sulphide of ammonium; this circumstance is frequently taken advantage of in the laboratory during the progress of an analysis, for the purpose of separating certain metals, the sulphides of which are soluble in solutions of the sulphides of the alkali-metals, from others which are insoluble. The following sulphides may be dissolved by a solution of ammonic sulphide, and by a solution of dipotassic sulphide:

Auric sulphide	...	Au_2S_3	Vanadic persulphide	...	V_2S_5
Platinic sulphide	...	PtS_2	Tungstic trisulphide	...	WS_3
Rhodic sulphide	...	Ro_2S_3	Molybdic trisulphide	...	MoS_3
Arsenious sulphide	...	As_2S_3	Molybdic tetrasulphide	...	MoS_4
Arsenic sulphide	...	As_2S_5	Stannous sulphide	...	SnS
Antimonious sulphide	...	Sb_2S_3	Stannic sulphide	...	SnS_2
Antimonic sulphide	...	Sb_2S_5	The sulphides of tellurium.		
Vanadic tetrasulphide	...	V_2S_4	The sulphides of iridium.		

The double salts thus obtained are decomposed by the addition of an acid, such as sulphuric or hydrochloric, sulphuretted hydrogen being evolved, and the sulphide of the electronegative metal precipitated; for example, $3Na_2S.Sb_2S_5+6HCl$ becomes $6NaCl+Sb_2S_5+3SH_2$, or $[2\mathbf{Sb}S(SNa)_3+6HCl=6NaCl+\mathbf{Sb}_2S_5+3\mathbf{S}H_2]$.

These electronegative sulphides are often soluble in solutions of the alkalies, forming a mixture of a sulpho-salt with an oxy-salt. Antimonious sulphide, for instance, when dissolved in a solution of potassic hydrate, gives the following result: $Sb_2S_3+6KHO=K_3SbO_3+K_3SbS_3+3OH_2$ $[\mathbf{Sb}_2S_3+6\mathbf{O}KH=\mathbf{Sb}(OK)_3+\mathbf{Sb}(SK)_3+3\mathbf{O}H_2]$.

Decompositions.—If free oxygen or atmospheric air be allowed

access to the heated sulphides, they are all decomposed; the sulphur becomes oxidized, and in most cases passes off as sulphurous anhydride, SO_2, whilst the metal remains in combination with oxygen. The sulphides of the metals of the alkalies and of the alkaline earths become converted into sulphates of the metal, and the same thing occurs less completely with many of the metals which have a strong attraction for oxygen; the sulphides of iron, lead, and copper are partially converted into sulphates, but by a stronger heat these sulphates afterwards lose their acid, and the oxide of the metal only is left. The sulphides of the noble metals, when roasted in a current of air, lose their sulphur, which burns off in the form of sulphurous anhydride, whilst the pure metal remains behind; in the case of silver, however, a portion of argentic sulphate is commonly formed.

Many of the hydrated sulphides are oxidized by exposure to the air, generally becoming converted into sulphates. The hydrated sulphide of iron, however, furnishes hydrated sesquioxide of the metal, whilst sulphur is liberated: and the sulphides of the metals of the alkalies and alkaline earths become converted into thiosulphates (hyposulphites); for instance, $2CaS + CO_2 + 2O_2 = CaS_2O_3 + CaCO_3$.

A large number of the sulphides, especially those of the more oxidizable metals, such as iron, zinc, and manganese, are dissolved by dilute hydrochloric acid in the cold, and still more readily when heated—a chloride of the metal being formed and hydrosulphuric acid evolved. Others, such as those of nickel, cobalt, and lead, require boiling with the concentrated acid: it is in this way that hydrochloric acid acts upon antimonious sulphide: $Sb_2S_3 + 6HCl$ becoming $2SbCl_3 + 3SH_2$. Sulphuric acid, when diluted, acts in a similar manner upon the sulphides of the more oxidizable metals, although less readily than hydrochloric acid.

The sulphides are all decomposed when heated in a current of chlorine gas, chloride of sulphur, and chloride of the metal being formed. This property is sometimes made use of in the analysis of ores consisting chiefly of sulphides, or of sulphides and arsenides of the metals; the volatile metallic chlorides are in this way separated from the more fixed ones. Aqua regia attacks and decomposes the sulphides as readily as gaseous chlorine; and a mixture of hydrochloric acid with potassic chlorate is equally effectual. Nearly all the metallic sulphides are readily decomposed by iodine, if suspended in water, and in a fine state of division; in most cases sulphur is set free, and a metallic iodide

is formed. With the exception of mercuric sulphide, they are also decomposed by nitric acid, sulphuric acid and a nitrate of the metal being formed; during this operation part of the sulphur is often separated in the form of tough elastic masses, which, if the heat be continued, collect into yellow globules, and can be oxidized only by prolonged digestion in the acid.

When the sulphides are fused with the alkaline carbonates or with the hydrated alkalies, they are partially decomposed, and the mass contains a variable mixture of sulphide with oxide of the alkali-metal, and different oxysalts of sulphur.

Before the blowpipe, the sulphides are easily recognized by the odour of sulphurous anhydride which they emit, either when heated in a glass tube open at both ends, or when roasted upon charcoal. Some other particulars relating to the sulphides have been already mentioned (416).

Preparation.—The sulphides can be prepared by various methods. 1.—Sulphur may be heated with the metallic oxides, many of which it decomposes: with the alkalies and alkaline earths, a sulphate, and a sulphide with variable proportions of sulphur are obtained; but when definite and pure sulphides are required, other means should be adopted. 2.—The lowest sulphides of the metals of the alkalies and alkaline earths may be prepared by igniting their sulphates in closed vessels with charcoal; oxygen is removed by the carbon, forming carbonic oxide, whilst the sulphide remaining may be dissolved out by water and filtered from the excess of charcoal; $K_2SO_4+4C=K_2S+4CO$. 3.—Hydrogen is sometimes employed for preparing the sulphides from the sulphates, which are placed in a tube and ignited in a current of the gas. In this manner the protosulphides of the alkali-metals are easily obtained, but the sulphates of the other metals frequently lose a portion of their sulphur, as well as all their oxygen, forming subsulphides. 4.—Many of the metals combine directly with sulphur, if heated with it, forming sulphides, but the compounds thus obtained often contain sulphur dissolved in, or disseminated through, the mass. Ferrous sulphide is usually prepared in this manner. Vermilion and realgar are also frequently prepared by the direct union of their constituents. Indeed, sulphur, although itself combustible, supports the combustion of many metallic bodies, which burn vividly when heated in its vapour. 5.—In other cases the sulphides may be formed by heating the metal in a current of sulphuretted hydrogen, or in the vapour of carbonic bisulphide. This latter method is the plan commonly adopted in preparing titanic sul-

phide from titanic anhydride; $TiO_2 + CS_2 = TiS_2 + CO_2$. 6.—Hydrated sulphides of the metals of the last three groups may also be obtained as insoluble precipitates, by passing sulphuretted hydrogen through neutral or acid solutions of their salts. 7.—The hydrated sulphides of zinc, iron, manganese, cobalt, and nickel are not thrown down by sulphuretted hydrogen in acidulated solutions, but can be prepared by double decomposition, by mixing a neutral solution of the salts of any of these metals with that of a sulphide of one of the alkali-metals: thus manganous sulphate if mixed with dipotassic sulphide yields potassic sulphate and manganous sulphide. $MnSO_4 + K_2S.xOH_2 = K_2SO_4 + MnS.xOH_2$. In many cases the colours of these hydrated sulphides are characteristic of the metal: for example, the hydrated sulphide of zinc is white; that of manganese flesh-red; those of cadmium and arsenicum are yellow, as is also stannic sulphide; and hydrated stannous sulphide is chocolate brown. The sulphides of molybdenum, rhodium, iridium, and osmium are brown, each with its peculiar shade; whilst in a large number of instances—including the sulphides of iron, cobalt, nickel, uranium, vanadium, bismuth, copper, lead, silver, mercury, gold, platinum, and palladium—the precipitated sulphides are of a black, more or less pure.

(569) **Estimation of Sulphur in Metallic Sulphides.**—Sulphur is always estimated in the form either of a sulphate or of free sulphur. The sulphur in a sulphide is easily converted into a sulphate by the agency either of gaseous chlorine or of aqua regia; and the soluble sulphates, when mixed in slightly acid solution with a salt of barium, yield the insoluble baric sulphate, the amount of which, after it has been well washed with boiling water and ignited, furnishes data for the calculation of the sulphur; 100 parts of baric sulphate representing 34·34 of sulphuric anhydride, or 13·73 of sulphur. If a salt of silver be present, baric nitrate must be employed to precipitate the sulphuric acid.

If during the solution of a sulphide in aqua regia, the sulphur has collected into clear yellow balls, and the action upon the ore appears to be complete, it is not necessary to wait until the whole of the sulphur is dissolved: the undissolved portion may be collected on a small counterpoised filter and weighed, and its amount must be added to that which has been converted into sulphuric acid, the proportion of which is to be ascertained by means of a barium salt in the manner above described.

(570) **SELENIDES** and **TELLURIDES.**—These are closely analogous to the sulphides in general characters, but they are too

rare to need particular description. The presence of selenium in a compound is readily ascertained by the peculiar odour which it emits when heated in the reducing flame of the blowpipe.

(571) **NITRIDES.**—It is not improbable that the fulminating compounds, obtained by digesting the hydrated oxides of gold, of silver, and of platinum, in a solution of ammonia, may owe their explosive character to the formation of a nitride: but the composition of these bodies has been only imperfectly investigated, on account of the readiness with which they explode. So weak is the chemical attraction of nitrogen for most metallic bodies, that a slight alteration of circumstances often suffices to restore it suddenly to the gaseous state. Nitride of copper is formed by passing dry ammonia over cupric oxide, at a temperature not exceeding 250° (482° F.), in which case water is formed at the expense of the hydrogen of the ammonia and the oxygen of the oxide, and part of the nitrogen escapes; thus, $6CuO+4NH_3=Cu_6N_2+6OH_2+N_2$. Nitrides of mercury and iron may be prepared by passing ammonia over mercuric and ferric oxide in a similar manner. Titanium, molybdenum, and vanadium absorb nitrogen rapidly at a red heat; and crystalline nitrides of chromium and magnesium have also been obtained.

(572) **PHOSPHIDES.**—The phosphides of the metals are of comparatively small importance: they are never met with in the native state. The phosphides of the metals of the alkalies and alkaline earths decompose water when thrown into it; self-lighting phosphuretted hydrogen is disengaged, and a hypophosphite of the metal remains in the solution. In some cases, as for example in that of calcic phosphide, the phosphide is formed by heating the oxide strongly, and passing the vapour of phosphorus over it; in this case it is mixed with a large proportion of calcic phosphate: other phosphides, as those of zinc and cadmium, may be prepared by the action of phosphorus on the heated metal. The insoluble phosphides may often be obtained by passing a current of phosphuretted hydrogen through a solution of the corresponding salt; phosphides of copper and mercury may be thus obtained.

When heated in air, phosphides are converted into phosphates, or the metal is liberated and phosphoric anhydride is formed.

(573) **CARBIDES.**—The only carbides of importance are those of iron, which will be considered in detail when treating of that metal. Manganese, palladium, iridium, and a few other metals, also combine with carbon; generally speaking, these carbides are more fusible than the metals themselves.

Silicon and boron form analogous compounds with the metals, but they are generally of small importance. Amongst the most interesting of the silicides are those of calcium, aluminium, magnesium, iron, and copper.

§ III. HYPOTHESIS ON THE CONSTITUTION OF SALTS.

(574) **ACIDS AND BASES.**—It has already been stated (6) that any substance which is produced by the action of an acid upon a base is termed a salt. It is, however, necessary to examine more minutely into the nature both of bases and acids, and into that of the compounds formed by their action upon one another.

By the word *base*, is meant a body always of a compound nature, most frequently an oxide of a metal, which is capable of effecting a double decomposition with an acid, whilst a salt and water are formed, and the distinctive characters of the acid are neutralized more or less completely. A base, however, is not necessarily a metallic oxide; the hydrates of ammonia, quinine, and morphine, for example, are powerful bases, but they contain no metallic substance.

(575) **Oxyacids and Hydracids.**—When Lavoisier gave the name of oxygen to one of the constituents of the atmosphere, he supposed that the presence of that energetic body was essential to the existence of an acid; and this view was rendered highly probable from a consideration of the composition of the principal acids then known, such as sulphuric, sulphurous, nitric, carbonic, phosphoric, and boracic acids. The term acid was indifferently applied to the anhydrides and to the compounds produced by the union of the anhydrides with water, to which latter class of compounds the term is restricted by many later writers, and to which it is applied in this work. Lavoisier considered an acid to be an oxidized body more or less soluble in water, with a sour taste, capable of reddening vegetable blues, and entering into combination with the alkalies, the distinctive properties of which it neutralized.

By degrees, however, acids were discovered into the composition of which hydrogen entered, but in which no oxygen could be detected: such, for example, as hydrochloric, hydriodic, and hydrobromic acids; yet these bodies were found in other respects to correspond perfectly with Lavoisier's definition, and to possess all the characters of powerful acids. To meet this objection, the theory was modified, and the acids were divided into two great classes, the first of which comprised the *oxyacids*, such as sul-

phuric, nitric, and others of analogous composition, in which it was supposed that the acid properties depended on the presence of oxygen; the second class was formed by the *hydracids*, such as hydrochloric and hydriodic acids, in which hydrogen was an essential component. It was noticed, that when bodies belonging to either of these classes combine with metallic compounds, and form neutral combinations, the acids do not unite directly with the metals without evolution of gas; with their *oxides*, on the contrary, combination appears to take place directly: dilute sulphuric acid, for example, has no action upon metallic copper, but it quickly dissolves its oxide, forming a blue solution of cupric sulphate. On applying heat so as to render the salt anhydrous, it was found that the salts of the oxyacids of which sulphate of potash, $KO.SO_3$, may be taken as the type (employing for the present the equivalents $O=8$, $S=16$, and the old notation), might be represented under the form $MO.SO_3$, which supposes the union of 1 equivalent of the anhydride with 1 equivalent of a metallic oxide; whilst a hydracid, if made to act upon a base yields a body, which when dry contains neither hydrogen nor oxygen, the radicle of the acid being left in combination with the metal itself: thus hydrochloric acid, HCl, and caustic soda, $NaO.HO$, yield common salt, $NaCl$: $NaO.HO+HCl=NaCl+2HO$. Thus, in the case of the salts of the hydracids, it will be observed that the oxygen of the oxide is precisely sufficient to convert the hydrogen of the acid into water: this union, indeed, actually takes place, and the water so formed is expelled on the application of heat. When, therefore, a hydracid acts upon a base, a true double decomposition occurs.

In consequence of this supposed difference in constitution, it was proposed to subdivide salts into two classes,—the first, like nitrate of potash, $KO.NO_5$, being formed by the union of an *oxyacid*, or anhydride as we now term it, such as the nitric, with an oxide such as potash; these were termed *oxysalts*: the other class being produced by the combination of a metal with the characteristic element in a hydrogen acid. The salts of the second class, being composed upon the same plan or type as sea-salt, were termed *haloid* salts (from ἅλς, sea-salt). This distinction is still recognized by many chemical writers. The supposition that a salt consists of an anhydride united to a base still affords the simplest explanation of many chemical decompositions; and it is difficult to represent many of the complex silicates satisfactorily by any other plan.

(576) **Binary Hypothesis of Salts.**—The foregoing observations seem to prove that there is a marked difference between the composition of the oxyacid and the hydracid series of salts. The separation of salts into two classes, one consisting of the salts of the oxyacids, and the other of those of the hydracids, is not, however, indispensable. A hypothesis was advanced by Davy and by Dulong, which reduces all salts to one type. According to this view—frequently termed *the binary theory* of salts—all the hydrated acids are regarded as *hydrogen salts*, that is, as salts containing hydrogen in the place of a metal, so that hydrogen acts the part of a feeble basyl towards a group of elements, or a single element, which forms the radicle of the salt. It has already been shown that the anhydrides of those oxyacids which can be obtained in an isolated form, such, for example, as sulphuric, nitric, phosphoric, carbonic, and boracic anhydrides, do not possess the properties generally assigned as constituting the true acid character. Sulphuric anhydride, for instance, does not redden dry litmus; it may be moulded in the fingers without injury; but when once it has united with the elements of water and passed into the hydrated form, it corrodes all organized substances with great activity. Carbonic anhydride is also without action on litmus. When such compounds have entered into combination with water they may be represented as hydracids, by a slight modification of the old formula; *e.g.*, nitric acid, $HO.NO_5$, may be expressed as $H.NO_6$, corresponding to hydrochloric acid, $H.Cl$: each equivalent of these bodies, when heated in contact with a base or a metallic oxide, gives off 1 equivalent of water, in a manner precisely analogous to the hydracids already examined. One equivalent of oil of vitriol treated with 1 equivalent of oxide of lead would thus produce an equivalent of sulphate of lead and an equivalent of water; $H.SO_4+PbO$ becoming $Pb.SO_4+HO$.

Most chemists indeed now regard the compounds which were previously considered as *hydrated acids* as salts composed of a compound radicle, which may be termed the *oxion* of the salt (consisting of the anhydride + oxygen) united with hydrogen. The other salts of the acid would be formed from these hydrogen salts by the displacement of the hydrogen by an equivalent amount of each of the different metals which enter into the composition of the various salts, and which are indicated by their respective names. In accordance with this view, we have already given a simple explanation of the liberation of hydrogen when dilute sulphuric acid is acted upon by zinc; the zinc merely

entering into combination with sulphion, and displacing the hydrogen; so that (resuming the notation which regards O=16 and water OH_2) H_2SO_4+Zn become $ZnSO_4+H_2$; and the reaction is, upon this view, analogous to that of the same metal upon hydrochloric acid; $2HCl+Zn=ZnCl_2+H_2$: in the one case the hydrogen in the hydric sulphate, and in the other that in the hydric chloride being displaced by the metal zinc.

A comparison of a few of the so-called hydracids with some of the hydrated oxyacids will show the analogy between them; whilst the corresponding anhydrides will be at once seen to belong to an entirely distinct group of compounds:

Hydracids.	Hydrated oxyacids.	Anhydrides.
Hydrofluoric acid HF	Nitric acid ... HNO_3	N_2O_5
Hydrochloric „ HCl	Hypochlorous acid HClO	Cl_2O
Hydriodic „ HI	Iodic „ $H_2I_2O_6$	I_2O_5
Hydrobromic „ HBr	Sulphuric „ H_2SO_4	SO_3

A few reactions between certain bases on the one hand with some of the hydracids, and on the other with certain hydrated oxyacids, will enable us to complete the parallel:

$$\begin{array}{rcrcrcl} 2HCl & + & Ag_2O & = & 2AgCl & + & OH_2 \\ 2HF & + & Ca''O & = & Ca''F_2 & + & OH_2 \\ HI & + & KHO & = & KI & + & OH_2 \end{array}$$

$$\begin{array}{rcrcrcl} 2HNO_3 & + & Tl_2O & = & 2TlNO_3 & + & OH_2 \\ H_2SO_4 & + & NaHO & = & NaHSO_4 & + & OH_2 \\ H_2SO_4 & + & Pb''O & = & Pb''SO_4 & + & OH_2 \end{array}$$

In each case the salt is formed by the substitution of an equivalent amount of metal for hydrogen, whilst a corresponding quantity of water is liberated in place of the metallic oxide originally employed.

Binary compounds are such as consist of single atoms of two elements only; sodic chloride, NaCl, therefore, is a binary compound; and if all salts be assimilated to this type, it is assumed that the grouping of their molecules resembles that which occurs in this binary compound. It has indeed been supposed that all salts consist of two portions: one comprising the distinctive constituents of the acid, and consisting either of a non-metallic elementary substance (chlorine, Cl, for example), which is termed the *radicle* of the salt, or else of a corresponding compound body (such as sulphion, SO_4), which may be conveniently distinguished as the *oxion* in cases where the acid contains oxygen; the other,

is either a metal (sodium, Na, for instance), or else a compound like ammonium, NH_4, equivalent to a metal, termed the *basyl* of the salt. It is easy to distinguish the oxions of acids in *ic* from those of acids in *ous*; by using in the latter case the termination *osion*; SO_3, the oxion of the sulphites being *sulphosion*, NO_2, the oxion of the nitrites, *nitrosion*, and so on. Attention has already been directed to the bearing of the electrolysis of saline compounds (286), upon this theory of their constitution.

(577) **Objections to the Binary Hypothesis.**—Notwithstanding the ingenuity of the foregoing hypothesis, and the advantages which it offers in the explanation of certain modes of decomposition, it is open to many serious objections; and indeed it cannot be regarded as a correct representation of the composition of a salt under all circumstances. In fact, none of the compound radicles or oxions, SO_4, NO_3, CO_3, have ever been obtained in an isolated form, nor is it likely that they will be.

It also appears to be highly improbable that a body of such powerful chemical attractions as potash should, in potassic carbonate for example, part with its oxygen to a substance which, like carbonic anhydride, exhibits no tendency to further oxidation, so that $K_2O.CO_2$ should become $K_2.CO_3$, or in the production of ammonic chloride, NH_4Cl, by the union of ammonia, NH_3, and hydrochloric acid, HCl, that the hydrogen of the hydrochloric acid should leave the chlorine for which it has such a powerful affinity to unite with the ammonia which has no appreciable attraction for hydrogen.

The conclusion which is most probable is this: viz., that a salt, when once formed, must be regarded as a whole; it can no longer be looked upon as consisting of two distinct parts, but as a new substance, maintained in its existing condition by the mutual actions of all the elements which compose it. These different elements are not all united with each other in every direction with an equal amount of force. As in a crystal there are certain directions in which the mass admits of cleavage with greater facility than in others, and as two or three different directions of cleavage may be found in the same crystal by varying the direction in which the force is applied, so in the same salt there are directions in which it yields to the application of chemical force more readily than in others; and according as that chemical force is applied in one way or in another, the compound splits up into simpler substances, the nature of which will vary according to the mode which has been selected for effecting its decomposition.

For example, if the solution of a powerful acid, such as nitric

acid, be poured upon potassic carbonate, carbonic anhydride is liberated, and potassic nitrate is produced; $K_2CO_3 + 2HNO_3 = 2KNO_3 + CO_2 + OH_2$; but if another portion of the same potassic carbonate be mixed with charcoal, and heated in an iron retort to whiteness, metallic potassium and carbonic oxide are the results; $K_2CO_3 + 2C = K_2 + 3CO$. Again, if a solution of potassic carbonate be subjected to electrolysis by the aid of the voltaic battery, the salt splits up into potassium (which is immediately oxidized by the water in the midst of which it is liberated), and into 'carbion,' CO_3, which is as instantly resolved into oxygen gas and carbonic anhydride; $2K_2CO_3$ becoming $2K_2 + 2CO_3$, and $2K_2 + 4OH_2$ give $4KHO + 2H_2$, whilst $2CO_3$ becomes $2CO_2 + O_2$. The probability therefore is, that neither the old nor the new view is absolutely correct, but that each may in turn be employed to represent the salt when subjected to the influence of particular circumstances. In certain cases therefore it is evident that the binary theory may elucidate the decompositions observed, notwithstanding the difficulties which prevent its adoption as a correct statical representation of the molecular arrangement of saline compounds. On the other hand, certain salts may occasionally be represented as compounds of the anhydride and the base: calcic carbonate, for example, may be written $CaO.CO_2$, although the empirical formula $CaCO_3$ will generally be most convenient. So, again, in the case of the sulphates. Anhydrous magnesic sulphate may, for instance, be often written $MgO.SO_3$, although we generally adopt the form $MgSO_4$, which involves no theory of its constitution. Constitutional formulæ as employed to indicate the composition of salts, and which aim at explaining the functions of the different atoms of which they are composed, have been already described (337).

(578) **Sulpho-Salts.**—The preceding remarks have been made almost exclusively with reference to those salts into the composition of which oxygen enters. There is, however, a numerous series of compounds parallel to these oxy-compounds, in which sulphur enters into combination with the metal; each atom of oxygen in the series of the oxy-salts being replaced by an atom of sulphur in the corresponding compound in the sulphur series. Generally speaking, the sulphur-salts are of subordinate importance to the oxy-compounds; many of them are decomposed by water, and they have been the subject of much less study and research than the oxy-salts. Many chemists regard these compounds as salts in which the electropositive sulphides, such as the protosulphides of potassium, &c., act the part of bases; and

the electronegative sulphides, such as the higher sulphides of arsenic and antimony, act as acids. No doubt their molecular constitution is analogous to that of the oxy-salts.

(579) **Varieties of Salts.**—Salts are usually spoken of as *neutral, acid,* or *basic;* but although these terms are in general use, there is considerable ambiguity in the manner in which they are applied.

(580) **Neutral, or Normal Salts.**—The idea of neutrality implies that the peculiar characters both of the acid and of the alkali have disappeared as a result of chemical combination, and one of the usual means by which this neutralization is judged of, consists in observing the effect which is produced upon certain vegetable colours by a solution of the salt.

The blue colour of litmus, for example, is changed to red by the action of an acid, whilst the colour of litmus reddened by an acid becomes blue if it be mixed with an alkali. The yellow colour of turmeric is changed to brown when mixed with an alkali, but the yellow is restored if the alkali be caused to combine with an acid. A salt which affects neither the blue of litmus nor the yellow of turmeric is said to have a neutral reaction. But chemists are in the habit of regarding many salts as neutral in composition, which are not neutral in their action upon coloured tests. The basic properties of different metallic oxides vary considerably in intensity. Equal quantities of the same acid, according as it is neutralized by equivalent quantities of a weak base or of a strong one, will differ considerably in their action upon coloured tests: for example, 62 parts of nitrion in combination with 39 parts of potassium furnish 101 of potassic nitrate, KNO_3, which, when dissolved in water, does not affect the colour either of blue or of reddened litmus-paper. It is therefore neutral in its reactions upon coloured tests.

Salts of nitric acid in which 1 atom of a monad like potassium, sodium, or silver displaces the hydrogen in 1 molecule of the acid, HNO_3, or in which 1 atom of a dyad such as lead or copper displaces the hydrogen of 2 molecules of nitric acid, $2HNO_3$, are regarded as neutral in composition, whatever may be their action upon vegetable colours. If, for instance, 223 parts of plumbic oxide, PbO, be made to act upon 126 parts of nitric acid, plumbic nitrate and water will be formed; $Pb''O + 2HNO_3 = OH_2 + Pb''2NO_3$, and the salt is neutral in composition, although if dissolved in water it reddens litmus, and has an acid reaction: the same thing is true, also, in the case of cupric nitrate, $Cu''2NO_3$. Thermo-chemical experiments seem to indicate that this acid

reaction of the aqueous solutions of certain salts is due to partial decomposition.

The change in the tint of the coloured test is therefore not to be regarded as a proof of neutrality or acidity in the composition of a salt. The change of colour which the litmus experiences, even from a salt of neutral composition, is readily explained. Blue litmus is itself a species of salt, containing one of the metals of the alkalies or alkaline earths, and formed from an organic compound by displacement of a part of the hydrogen; this compound, which is naturally of a red colour, becomes blue when it is neutralized by an alkali. When a powerful acid, such as nitric or sulphuric acid, is mixed with a solution of blue litmus, double decomposition takes place, a sulphate or nitrate of the metal is formed, and the organic compound of the litmus acid is set free and appears of its natural red hue; but on the addition of an alkali, the blue is restored by the reaction of the newly added base upon the litmus acid and the formation of the litmus salt of the alkali-metal. Again, if a salt with a strong oxion and a comparatively feeble basyl be mixed with the blue litmus, the strong oxion seizes upon a part of the basyl which is in combination with the litmus, and liberates the litmus acid, which appears of a more or less intense red, according as the basyl of the neutral salt has given up more or less of its oxion.

For analogous reasons it sometimes happens that a salt which is neutral in composition may exhibit characters in which the basyl preponderates to a greater or less extent. Common or dipotassic carbonate, K_2CO_3, is neutral in composition, but it appears to be basic in its action upon the yellow colour of turmeric paper, which it renders powerfully brown, and it immediately restores the blue tinge to reddened litmus. This ambiguity in the use of the word neutral, may, however, be entirely obviated by describing as *normal salts* the salts above-mentioned as neutral in composition; employing the term neutral solely with reference to the action of the body upon coloured tests; and in this sense these terms will be used hereafter. Frankland defines a normal salt as "one in which the displaceable hydrogen of the acid is all exchanged for an equivalent amount of a metal, or of a positive compound radical."

(581) **Polybasic Acids—Acid Salts.**—If a quantity of oxalic acid be divided into two equal portions, one of which is dissolved in water, and mixed with a solution of potassic hydrate until the liquid becomes neutral in its reaction upon litmus, a salt is formed, which, on evaporation, may be obtained crystallized in

six-sided prisms, consisting of the normal or dipotassic oxalate, $K_2C_2O_4.OH_2$. If this salt be redissolved in water, and the second portion of oxalic acid be added to it, chemical union of the two bodies will occur; the liquid so obtained will be found to have a sour taste, to redden litmus powerfully, and on evaporation to yield a new salt, which crystallizes in rhomboidal prisms, containing exactly half as much potassium in proportion to the acid as the first salt; this is the hydric potassic oxalate, commonly known as the binoxalate, or acid oxalate, of potassium, $KHC_2O_4.OH_2$; for $K_2C_2O_4.OH_2 + H_2C_2O_4.OH_2 = 2(KHC_2O_4.OH_2)$.

Again, if the normal or dipotassic sulphate, K_2SO_4, be dissolved in hot sulphuric acid, tabular plates of a new, fusible, and strongly acid salt, will crystallize out as the liquid cools, and the hydric potassic sulphate, commonly called the bisulphate or acid sulphate of potassium, $KHSO_4$, will be formed; for, $K_2SO_4 + H_2SO_4 = 2KHSO_4$. This salt contains only half the amount of potassium which is present in the normal sulphate. If an attempt be made to form a similar acid salt by dissolving potassic nitrate in nitric acid, the experiment will fail, for the nitre will be found to crystallize out unchanged.

The bodies now distinguished as acids, it must be remembered, are simply salts of hydrogen; and, from the experiments just described, it is apparent that there are certain acids in which their basic hydrogen admits of displacement by a metallic basyl in one proportion only, whilst there are other acids in which the hydrogen admits of displacement by a metal in two proportions, forming two classes of salts, one of which is neutral and the other acid. Such acid salts consequently contain, in addition to the oxion and basyl, a certain quantity of hydrogen, as occurs, for instance, in the acid sulphate and the acid oxalate of potassium. This hydrogen is not to be regarded as present in the form of water of crystallization: it discharges a more important function, for it takes the place of one of the atoms of the metal on these occasions; and the acid character predominates in such salts, because the acid is only partly neutralized by the metal.

Acids in the molecule of which but a single atom of hydrogen admits of displacement by an atom of a metallic monad, when this monad is presented to it in the form of a hydrate, are said to be *monobasic*. Hydrochloric acid, HCl, nitric acid, HNO_3, and acetic acid, $HC_2H_3O_2$, are examples of this class.

If, however, the molecule of the acid contains 2 atoms of hydrogen, susceptible of displacement by two atoms of a monad like potassium, or by one atom of a dyad like zinc, the acid is

said to be *dibasic*, like sulphuric acid, H_2SO_4, oxalic acid, $H_2C_2O_4$, and tartaric acid, $H_2C_4H_4O_6$. Many of the organic acids belong to this class.

Again, if the molecule of the acid contains 3 atoms of hydrogen susceptible of displacement by 3 atoms of a monad like potassium or silver, or by one atom of a triad like bismuth, such an acid is said to be *tribasic*. Orthophosphoric acid, H_3PO_4 (516), is a good instance of this kind, and among the organic acids, the citric, $H_3C_6H_5O_7$, may be mentioned; whilst pyrophosphoric acid, $H_4P_2O_7$ (517), may be cited as an example of a *tetrabasic* acid.

Acids which allow the substitution of more than one atom of hydrogen by a corresponding number of atoms of a metallic monad (whether 2, 3, or 4 atoms) are said to be *polybasic*.

Ordinary nitre affords an instance of a normal salt formed by the action of the hydrate of a metallic monad upon a monobasic acid, $HNO_3+KHO=KNO_3+OH_2$; plumbic nitrate, $Pb''2NO_3$ illustrates the case of a normal salt obtained by the reaction of the protoxide of a dyad metal upon a monobasic acid, $2HNO_3+Pb''O=Pb''2NO_3+OH_2$; and potassic sulphate affords an example of the formation of a normal salt by the reaction of the hydrate of a monad metal with a dibasic acid, $H_2SO_4+2KHO=K_2SO_4+2OH_2$. These three varieties include the most common forms of normal salt. When a dibasic acid acts upon the protoxide or hydrate, of a metallic dyad, a salt is produced similar to that obtained by the reaction of sulphuric acid upon calcic hydrate, where two atoms of hydrogen in the acid are replaced by 1 atom of the dyad calcium; $H_2SO_4+Ca''H_2O_2=Ca''SO_4+2OH_2$.

But numerous salts are known which are formed by the action of sesquioxides upon the acids. In certain cases the sesquioxides act upon the acids just as the protoxides do. For instance, the sesquioxides of antimony and uranium, as well as those of bismuth, iron, and aluminium, in certain circumstances yield a sulphate by the action of the two bodies in the proportions indicated in the following equations:

$$H_2SO_4+U_2O_3=(U_2O_2)''SO_4+OH_2$$
$$H_2SO_4+Sb_2O_3=(Sb_2O_2)''SO_4+OH_2$$
$$H_2SO_4+Bi_2O_3=(Bi_2O_2)''SO_4+OH_2$$
$$H_2SO_4+Fe_2O_3=(Fe_2O_2)''SO_4+OH_2$$
$$H_2SO_4+Al_2O_3=(Al_2O_2)''SO_4+OH_2$$

These sulphates, however, with the exception of the first, are all

insoluble; the oxide of uranium $(U_2O_2)''$, *uranyl*, as Péligot has termed it, has been isolated; indeed, it was for some years mistaken for metallic uranium, until Péligot proved that it contained oxygen. Bismuthyl $(Bi_2O_2)''$ has also been prepared, but the other oxides of the formulæ corresponding to uranyl have not as yet been isolated. The foregoing salts are generally regarded as basic salts, derived from the sesquioxides. Many of them are conveniently represented by the general formula $M_2O_3.SO_3$, or they may, by trebling the formulæ given above, be represented in the following manner; they often, however, retain water not indicated in these formulæ:

Basic antimonious sulphate	$Sb_23SO_4.2Sb_2O_3$
„ bismuth „	$Bi_23SO_4.2Bi_2O_3$
„ ferric „	$Fe_23SO_4.2Fe_2O_3$
„ aluminic „	$Al_23SO_4.2Al_2O_3$

In the majority of instances, when a dibasic acid, such as sulphuric acid, acts upon a sesquioxide, such as alumina or ferric oxide, three molecules of the dibasic acid are required to form a normal soluble salt, in which case the metal becomes trivalent, and two atoms of the metal are therefore equivalent to 6 atoms of hydrogen. For example, $3H_2SO_4 + (Al''')_2O_3$ yield $(Al''')_23SO_4 + 3OH_2$, and under these particular circumstances iron itself, instead of being bivalent, as in the ferrous salts, becomes trivalent in the ferric salts. $3H_2SO_4 + (Fe''')_2O_3$ yield $(Fe''')_23SO_4 + 3OH_2$; thus affording an example of the remarkable fact of a metal possessing two different values in its compounds.

Other metals besides iron behave in the same manner: chromium and cerium, for example, in particular cases may be bivalent, whilst in other cases they act as trivalent metals; for instance, they are bivalent in

Chromous chloride and sulphate	$Cr''Cl_2$; $Cr''SO_4$
Cerous chloride and sulphate	$Ce''Cl_2$; $Ce''SO_4$

and trivalent in

Chromic chloride and sulphate	Cr'''_2Cl_6; Cr'''_23SO_4
Ceric chloride and sulphate	Ce'''_2Cl_6; Ce'''_23SO_4

In the protoxides and salts corresponding to them, these metals are bivalent; whilst in the sesquioxides and the salts corresponding to them the metals are trivalent. Tin, platinum, and palladium, again, in certain cases are bivalent, in others quadrivalent. This subject will be further considered in the opening chapter of the third volume of this work.

The normal salts derived from these different sesquioxides by

the action of acids upon them have usually an acid taste, and redden litmus powerfully. This is well seen in the normal ferric and aluminic sulphates.

It is not necessary that the two or the three atoms of basyl which the salts of the dibasic or tribasic acids contain should consist of the same metal. Indeed, it has already been shown, in the case of the various phosphates, that several basyls may coexist in the same salt. In disodic dihydric pyrophosphate, for example, $Na_2H_2P_2O_7$, 2 atoms of hydrogen supply the place of 2 atoms of sodium; and in the microcosmic salt, $Na.NH_4.H.PO_4.4OH_2$, we have a tribasic sodic ammonic hydric phosphate, where each of the three atoms of basyl differs from the others.

Now it frequently happens that hydrogen is one of the basyls present in the salt, and when such is the case, the salt, when dissolved in water, usually has a sour taste, and reddens litmus-paper strongly. It is in this way that the most common variety of acid salts is formed, such as the so-called binoxalate and the bisulphate of potassium already adverted to (p. 391). Cream of tartar, or, as it is often called, bitartrate of potash, offers another good illustration of this kind of salt.

Cream of tartar is a sparingly soluble crystallizable compound, of an agreeable acidulous taste; it consists of $KHC_4H_4O_6$, and is, in fact, a dibasic potassic hydric tartrate: if now it be dissolved in hot water, and a molecule of potassic hydrate be added, the hydrogen is displaced by the second atom of potassium, all the acid taste disappears, and normal or dipotassic tartrate is produced, $K_2C_4H_4O_6$, a salt which no longer affects the colour either of litmus or of turmeric paper. An equivalent quantity of potassic carbonate may be substituted for potassic hydrate with equal effect, as it will be decomposed, and the carbonic anhydride expelled with effervescence. Sodic carbonate may be substituted for potassic carbonate, but in this case a different salt, known as Rochelle salt, the sodic potassic tartrate, $KNaC_4H_4O_6.4OH_2$, will be formed as represented in the following equation; $NaHCO_3 + KHC_4H_4O_6 = KNaC_4H_4O_6 + OH_2 + CO_2$.

Acid salts are generally formed like cream of tartar, from a dibasic acid which has reacted with one molecule only of a powerful monad base, whilst the place of the second atom of metal has been supplied by an atom of hydrogen; but they are not always so produced: the acid chromate of potassium, dichromate of potassium, $K_2CrO_4.CrO_3$, contains no hydrogen, and a sulphate of potassium, $K_2SO_4.SO_3$, of analogous composition has also been obtained; the latter, however, may be regarded as the

normal potassic salt of pyrosulphuric acid, $H_2S_2O_7$ (p. 217). Such salts have been distinguished from ordinary acid salts by the term *anhydro-salts*, or salts containing an anhydride.

(582) **Double Salts.**—The foregoing description of the polybasic acids has presented us with certain cases in which *double salts* are formed. There are several varieties of double salts, the most common being those which are produced by the union of two dissimilar metals with the same acid radicle or oxion. It is not possible to form double salts *ad libitum*, by bringing 2 equivalents of any acid in contact with 1 equivalent each of any two bases. Chemists assume that when two different metallic monads, such as sodium and potassium, combine with the same oxion in the proportion of 1 atom of each metal to form a double salt (like Rochelle salt), the acid in question is dibasic. The larger number of double salts which have been produced are thus formed by the combination of different metals with polybasic oxions. The so-called bicarbonates, binoxalates, and many other similar compounds are true double salts of this class, analogous to normal or neutral salts, in composition; but one-half of their basylous constituents consists of hydrogen. Some other considerations relating to the basicity of acids and to the polybasic acids will be more conveniently deferred until the nature of the organic acids has been discussed.

The formation of another remarkable series of double salts, particularly investigated by Graham, appears to be directly connected with the mode in which water attaches itself to certain salts. In most cases the water of crystallization may be expelled from a salt by exposing it to a temperature not exceeding that of boiling water. This, however, does not always happen: sometimes all the water of crystallization may thus be expelled with the exception of a single molecule, which requires a much higher heat for its expulsion; under these circumstances it was found that this last molecule of water might readily be replaced by a molecule of certain anhydrous salts. An excellent illustration of such a method of the formation of double salts is afforded in the case of a certain class of the sulphates. All the sulphates of metals isomorphous with magnesium are capable of forming double salts of this nature with some anhydrous sulphate not isomorphous with this class—such, for instance, as potassic sulphate.

When magnesic sulphate, $MgSO_4.OH_2$, $6OH_2$ is heated to 100° (212° F.), six out of the seven molecules of water are expelled, but the seventh molecule is retained until the temperature is

raised considerably. If, however, magnesic sulphate and potassic sulphate be separately dissolved in water in molecular proportions, mixed while hot, and allowed to crystallize, a new double salt, $MgSO_4.K_2SO_4, 6OH_2$, is deposited, having the same crystalline form as magnesic sulphate, but it contains only 6 molecules of water of crystallization. The seventh molecule has been displaced by the potassic sulphate, and this portion of water has been termed by Graham, constitutional, or *saline water*.

There is another well-known variety of double salts, in which it is not necessary that the component salts should be formed from oxides of the same class, or even contain a similar number of equivalents of the radicle of the acid. In this way sulphates formed from sesquioxides often unite with the sulphates formed from protoxides to produce well-characterized double salts: a striking example of this kind is afforded in the important class of alums. Common alum consists of a combination of potassic with aluminic sulphate and water of crystallization, $K_2Al_24SO_4.24OH_2$: numerous other salts, having the same crystalline form, and of analogous composition, are known.

There are a few instances of two different oxions or acid radicles being united to one basyl, but they are neither sufficiently numerous nor important to merit lengthened notice; they are more frequently met with among natural than artificial combinations.

Instances are common in which two different haloid salts unite with each other; compounds of this description are most usual between the chlorides, iodides, and bromides of the less oxidizable metals and those of the metals of the alkalies and earths: the potassic platinic chloride, $2KCl.PtCl_4$, and the potassic mercuric iodide, $2KI.HgI_2$, are good instances of such compounds. Bonsdorff proposed to consider these compounds in the light of salts in which the chloride or iodide of the electronegative metal (platinum, gold, &c.) acted the part of an acid towards the electropositive chloride (chloride of potassium, sodium, &c.); but this view is not tenable. Such salts are never resolved by electric action into their constituent chlorides, and the acid reaction of the higher chlorides is not neutralized or modified by combination with the chlorides of the alkali-metals; in fact, the constituent chlorides themselves are salts.

Many double salts may be formed by fusion with each other, although they cannot be procured by the usual method of crystallization from a solution containing equivalent quantities of the two salts. Sodic chloride, for example, may be melted with an

equivalent amount of calcic, strontic, or baric chloride; and in each case a compound salt is obtained, which has a much lower fusing-point than either of its component chlorides in a separate form; but the double salt is decomposed when it is dissolved in water.

(583) **Subsalts.**—A very different series of saline compounds still remains for consideration, and in these the proportion of base predominates over that of the acid; they are usually designated *basic salts,* or subsalts. The theory of the formation of these compounds is very imperfect. In many cases subsalts may be compared to salts which contain water of crystallization, the molecules of base in excess being assumed to be attached to the normal salt in a manner analogous to that by which the water of crystallization is retained in ordinary instances.

The tendency to the formation of subsalts is limited to certain acids and bases. It is indeed one of the peculiarities of the monad bases, such as the alkalies, and the oxides of silver and thallium, that they do not form basic salts; oxides of the dyads, such as the oxides of copper, lead, mercury, and zinc, have a strong tendency to do so, whilst the oxides of the triads, when basic, such as the sesquioxides of antimony and bismuth, have a still greater propensity to form basic salts. No general rule can be laid down for the acids, but among the common acids, those which most frequently form basic salts are the sulphuric, nitric, carbonic, and acetic acids.

Among basic sulphates, for example, are the following:

Brochantite	$CuSO_4.3CuH_2O_2$
Tribasic cupric sulphate	$CuSO_4.2CuH_2O_2$
Turpeth mineral	$HgSO_4.2HgO.$

Among basic nitrates are,

Dibasic plumbic nitrate	$Pb2NO_3.PbH_2O_2$
Tetrabasic cupric nitrate	$Cu2NO_3.3CuH_2O_2$
Mercurous subnitrate	$3(Hg_22NO_3).Hg_2H_2O_2$
De Marignac's do.	$3(Hg_22NO_3).2Hg_2H_2O_2.$

The following are instances of basic acetates:

Verdigris	$Cu2C_2H_3O_2.CuO.6OH_2$
Tribasic cupric acetate	$2(Cu2C_2H_3O_2).4CuO.3OH_2$
Tribasic plumbic acetate	$Pb2C_2H_3O_2.2PbO.OH_2$
Hexabasic plumbic acetate	$Pb2C_2H_3O_2.5PbO.OH_2.$

As examples of basic carbonates, we give,

Malachite	$CuCO_3.CuH_2O_2$
Blue carbonate of copper	$2CuCO_3.CuH_2O_2$
White lead	$2PbCO_3.PbH_2O_2.$

Just as we have polybasic acids, so are there polyacid basyls—basyls, that is, such as the dyads or triads, which require more than one atom of a monobasic oxion for their saturation This is the case, for example, with the metals of the alkaline earths; but as yet the class of double salts, which they form, has been scarcely examined.

(584) **Oxychlorides, &c.**—A class of compounds which resemble the subsalts more than any others, are the bodies termed oxychlorides, oxyiodides, and oxycyanides. In these compounds, one molecule of the chloride, of the iodide, or of the cyanide of a metal is united with one or more molecules of the oxide of the same metal. Turner's yellow, which is an oxychloride of lead, $PbCl_2.7PbO$, is a well-known commercial article belonging to this class. Such combinations usually occur between oxides and chlorides or iodides of metals, the pure chlorides or iodides of which never form any but anhydrous crystals.

Some salts enter into combination with other bodies, and form compounds which are in many respects anomalous; such for instance are the compounds of ammonia with many dry salts: 2 molecules of argentic chloride will in this manner absorb 3 molecules of ammonia. Many of the salts of copper exhibit a similar power (679).

CHAPTER XVII.

GROUP I.

METALS OF THE ALKALIES.

Metal.	Symbol.	Atomic weight.	Atomic volume.	Specific heat.	Fusing point. °C.	Fusing point. °F.	Density.	Electric conductivity, 68°—71° F.
Cæsium ...	Cs	133						
Rubidium	Rb	85·4	56·18		38·5	101·3	1·52	
Potassium	K	39·1	45·20	0·16956	62·5	144·5	0·865	20·85
Sodium ...	Na	23	23·66	0·29340	97·6	207·7	0·972	37·43
Lithium ...	L	7	11·80	0·94080	180·0	356·0	0·593	19·00

THE metals of this class are soft, easily fusible, and volatile at high temperatures; they furnish several oxides, of which only one is basic. This oxide is caustic, and extremely deliquescent: the hydrate cannot be decomposed by ignition; it absorbs carbonic anhydride with avidity. The carbonates are soluble, so are the sulphides and hydric sulphides (see pp. 352, 377).

§ I. **POTASSIUM** (Kalium) [K′=39·1] *Density*, 0·865; *Fusing-pt.* 144°·5 (62°·5 C.)

Native Compounds which contain Potassium.

Alum . . . . $K_2Al_24SO_4.24OH_2$.
Felspar . . . $(KNa)'_2O.Al_2O_3.6SiO_2$.
Biaxal mica . . $K_2O.3[(AlFe)'''_2O_3].6SiO_2$.

(585) **Formulæ of Mixtures of Isomorphous Compounds.**—The formulæ employed above for felspar and mica require explanation, as the principle of notation adopted in these cases will be applied hereafter to the formulæ of a large number of minerals.*

It often happens that isomorphous bases displace each other in the same mineral without altering its form or mineralogical characters, or even without altering its general chemical formula. Mica, for example, may be regarded as a compound of 1 molecule of a silicate of a protoxide of a metal with 3 molecules of a different silicate of a sesquioxide of a different metal. Let M′ stand for the metallic base of the protoxide, M‴ for the metallic base of the sesquioxide; the general formula for mica may then be expressed thus:

$$\text{Mica} = M'_2O.3SiO_2.3(M'''_2O_3.SiO_2).$$

Now the components of potash-mica are principally silicate of potash and silicate of alumina, the potash being the metallic protoxide, and the alumina being the metallic sesquioxide; but the sesquioxides of iron, manganese, and chromium are also isomorphous with alumina: these compounds frequently replace a portion of the alumina in its combinations, and this is especially the case with the sesquioxide of iron. The peculiarity of isomorphous metals, when they replace each other, is this—that the replacement may occur in *any* proportion; for example, in different specimens of mica the relative proportions of iron and aluminium are liable to great variations; this arises from the fact that the ferric silicate and aluminic silicate which are isomorphous, will crystallize together in any conceivable proportion, without altering the form of the mineral. The same fact can also be represented by stating that they may vary indefinitely in amount, provided only that the quantity of the two metals taken together in any one specimen furnishes such a proportion of a

* The formulæ of the silicates are so complex, and the true function of silica in combination is at present so ill-defined, that they in this work have been throughout formulated as containing silica in combination with the bases.

metallic sesquioxide as will saturate the silica in that portion of the mineral; that is, to say, that the 2 proportionals of metal required for combination with the 3 proportionals of oxygen in the sesquioxide, may either consist wholly of aluminium, or a *smaller or larger, but indefinite* proportion of the aluminium may have its place supplied by an *equivalent* quantity of iron.

Now the method of notation adopted in the preceding formulæ is employed to indicate precisely this—that the proportions of the two or more metals, the symbols of which are bracketed together, thus, $(AlFeMn)'''_2O_3$, are liable to vary within any conceivable limits, provided that the united amount of all the metals so bracketed be exactly sufficient to form a true sesquioxide with the three proportions of oxygen.

In like manner, in the case of the potassium in felspar, the place of part of the potassium may be supplied by sodium; but the proportions of the two taken together require exactly the same amount of oxygen as 1 molecule of potassium, and consequently saturate the same proportion of silica, that 1 molecule of potassic oxide alone would have required.

This frequent partial displacement of one isomorphous metal by another in native crystallized minerals, renders much caution necessary in interpreting the results of an analysis. The difficulty of fixing the formula of a mineral of course increases with the complexity of its composition, and it is with the silicates especially that these difficulties are experienced. It is usual, when the analytical operations are completed, to ascertain the proportion of oxygen in the silica, then the proportion of oxygen contained in the sesquioxides, and lastly the quantity of oxygen in the protoxides; because, however much the proportions of the different metals may vary in different specimens of the same mineral, the ratio of the oxygen in both sets of bases to the oxygen in the silica remains uniform. In felspar, for instance, if the proportion of oxygen in the silica be taken as 12, that in the sesquioxide of aluminium is 3, and that in the protoxide of potassium or sodium is 1.

(586) **POTASSIUM.**—This remarkable metal was discovered by Davy, in the year 1807, and its isolation marks an important era in the progress of philosophical chemistry. The alkalies and the earths had long been suspected to be compound bodies, but up to that period they had resisted all attempts to decompose them. When once potassium, however, had been separated from its compounds, and potash had been proved to be an oxide of this metal, the decomposition of the other alkalies and earths fol-

lowed as a necessary consequence: more correct ideas upon fundamental points of chemical theory were introduced; new methods of research were placed within reach of the analytical chemist, and potassium itself, from its powerful attraction for oxygen, became an important addition to the reagents of the laboratory.

(587) **Preparation of Potassium.**—1. Davy originally obtained potassium by decomposing a fragment of potassic hydrate (which had become slightly moistened upon its surface by exposure to the air for a few minutes) by the current of a Wollaston's voltaic battery of 200 or 250 pairs of plates, 6 inches (15 centim.) square. (*Phil. Trans.*, 1808, 4). The dry hydrate is an insulator, but a trace of moisture confers upon it a sufficient degree of conducting power; under such circumstances globules of metallic potassium are separated at the negative wire, and may be preserved under naphtha. They burn vividly in the air, leaving an intensely alkaline residue. This method of procuring the metal however is difficult and expensive, and only furnishes it in very small quantity.

2.—Gay-Lussac and Thénard, in 1808, invented a method by which potassium may be obtained by purely chemical means in greater abundance. Iron turnings were heated to whiteness in a curved gun-barrel, which was covered with a clay lute, to preserve it from the action of the air at a high temperature, and melted potassic hydrate was allowed to pass slowly over the ignited iron; decomposition ensued, the iron combined with the oxygen, setting free the potassium and the hydrogen, the former of which was condensed in a well-cooled copper receiver.

3.—The process by which potassium is now obtained consists in decomposing its carbonate by charcoal, a plan originally invented by Curaudau, and improved by Brunner. This operation has been carefully studied by Mareska and Donné (*Ann. Chim. Phys.*, 1852, [3], xxxv. 147). In order to ensure a successful result, attention to a number of minute precautions is requisite. The material which is best adapted to its preparation is the potassium salt of some vegetable acid, which, when decomposed by heat in a vessel from which air is excluded, leaves a large quantity of carbon.

For this purpose hydric potassic tartrate (crude tartar) is preferred. About 3 kilos. or 7 lb. of this substance is placed in a capacious iron crucible furnished with a cover, and ignited until it ceases to emit combustible vapours. A porous mass of potassic carbonate, intimately mixed with very finely divided carbon, is thus obtained: this is rapidly cooled by moistening the exterior of the crucible with cold water; the charred mass, when cold, is broken up into lumps of about

the size of a hazel-nut, and quickly introduced into a wrought-iron retort, which is usually made of one of the iron bottles in which mercury is imported; this is introduced into a furnace, *a*, as shown at *b*, fig. 336, and placed horizontally upon supports of fire-brick, *ff*; a wrought-iron tube, *d*, $4\frac{1}{2}$ inches (or 11 centi-

FIG. 336.

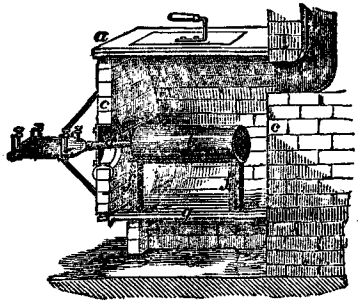
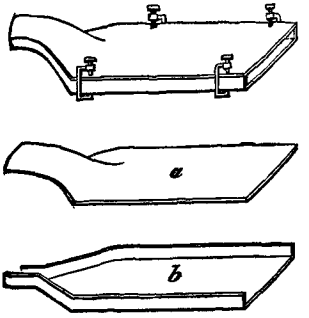


FIG. 337.



metres) long, serves to convey the vapours of potassium produced during the distillation into a receiver, *e*, which it is found most advantageous to construct of the form shown on an enlarged scale in fig. 337. It consists of two pieces of wrought-iron, *a*, *b*, which fit closely to each other, so as to form a shallow box only a quarter of an inch ($6^{mm.}$) deep, and are confined in their places by clamp screws: the iron plate should be $\frac{1}{6}$ in. ($4^{mm.}$) thick, 12 in. ($30^{cm.}$) long, and 5 inches (or $12^{cm.}$) wide; the receiver is open at both ends, the socket fitting upon the neck of the iron retort. The object in having the receiver of this particular form is to ensure the rapid cooling of the potassium, and so to withdraw it from the action of the carbonic oxide which is disengaged during the whole process; for heated potassium readily unites with carbonic oxide, giving rise to a dangerously explosive compound. Before this receiver is connected with the tube, *d*, the fire is slowly raised until the retort attains a dull red heat; powdered vitrified borax is then sprinkled over its exterior; the borax melts, and forms a coating which protects the metal from oxidation. The heat is then urged until it becomes very intense. A mixture of coke and charcoal forms a fuel well adapted to this purpose, and care should be taken that the temperature of the furnace should be as uniform as possible in every part. When a full reddish-white heat is attained, vapours of potassium begin to appear, and burn with a brilliant flame: the receiver is now adjusted to the iron neck of the retort, which is not allowed to project more than a quarter of an inch ($6^{mm.}$) through the iron plate which forms part of the front wall, *c*, of the furnace, lest the tube should become obstructed by the accumulation of solid potassium. Should any obstruction occur, it must be removed by thrusting in an iron rod; if this fails, the fire should be immediately withdrawn; this is readily effected by removing the fire bars, *g*, from the furnace, with the exception of the two which support the retort; the fuel thus falls into the ashpit. The receiver is kept cool by the application of a wet cloth upon its exterior. When the operation is complete, the receiver containing the potassium is removed, and instantly plunged into a vessel filled with rectified Persian naphtha, and provided with a cover. The vessel is kept cool by immersion in water. When the receiver is sufficiently cold, the potassium is detached, and preserved under naphtha.

In order to obtain the maximum produce of potassium, it is necessary that the mixture of potassic carbonate and carbon

should contain 1 molecule of the carbonate to 2 atoms of carbon, or 138 parts of the carbonate by weight to 24 of carbon. Upon the application of heat the mixture is wholly converted into carbonic oxide and potassium; $K_2CO_3 + C_2 = K_2 + 3CO$. The charge usually yields about one-fourth of its weight of crude potassium, some loss during the process being inevitable. Mareska and Donné found this loss to amount to about one-third of the entire quantity of the metal contained in the charge.

The potassium thus obtained is not pure, so that it is necessary to subject it to a second distillation in an iron retort; a little naphtha should likewise be introduced, which vaporizing as the retort is heated, expels the air and preserves the metal from oxidation. This redistillation is *essential;* for, if it be neglected, a black detonating compound is speedily formed by exposure to the atmosphere, and is even produced spontaneously, although the metal be kept under naphtha; this substance explodes violently upon the slightest friction. The purified metal amounts to about two-thirds of the quantity operated on. A third distillation may be necessary, if the potassium be required in a state of perfect purity. A little impure potassium almost always remains in the tube attached to the retort; and in order to prevent the possibility of the formation of the detonating compound already mentioned, it is best to detach this tube as soon as it is cold, and to immerse it in water.

(588) **Properties of Potassium.**—Potassium is a bluish-white metal, which is brittle, and has a crystalline fracture at 0° (32° F.); at temperatures a little above this it is malleable: at 15° (59° F.) it is soft; as the temperature rises it becomes pasty, and at 62°·5 (144°·5 F.) it is completely liquid. Whilst in the soft condition, two clean surfaces of the metal admit of being welded together like iron; at a red heat it may be distilled, and it yields a beautiful green vapour. Potassium is light enough to float in water, having a density of only 0°865. If exposed to the air, even for a few minutes, it becomes covered with a film of oxide, and when heated to its point of volatilization it bursts into flame, and burns with great violence. The powerful attraction which potassium has for oxygen is well shown by its action on water: on throwing a piece of the metal on to water, the latter is immediately decomposed: each atom of potassium displaces one half the hydrogen in a molecule of water, forming potassic hydrate, $2OH_2 + K_2 = 2KHO + H_2$, whilst the escaping hydrogen becomes ignited by the intense heat developed by the reaction, and burns with a beautiful rose-red flame; the melted metal swims about rapidly

upon the surface of the water, finally disappearing with an explosive burst of steam, when the globule of melted potassic hydrate which is formed becomes sufficiently cool to come into contact with the water. Potassium decomposes nearly all gases which contain oxygen, if it be heated in contact with them, and at a high temperature it will remove oxygen from almost all compounds which contain that element. It becomes necessary therefore to preserve the metal either in exhausted hermetically sealed glass tubes, or under the surface of some liquid, like naphtha, which does not contain oxygen. Potassium is soluble in liquefied ammonia, forming a blue liquid which deposits the metal in crystals as it evaporates. Potassium enters directly into combination with the halogens, and with sulphur, selenium, and tellurium, burning vividly when heated with them. It likewise absorbs carbonic oxide with facility when heated moderately in it, or when the vapour of potassium is allowed to condense slowly in an atmosphere of the gas: a dark-red compound, $K_2C_2O_2$, is thus formed from which the metal cannot be recovered; it furnishes potassic rhodizonate when treated with water, and occasions considerable waste in the ordinary method of preparing potassium.

(589) **POTASSIC HYDRIDE**, $KH_2 = 41{\cdot}1$.—When potassium is heated in an atmosphere of hydrogen, the gas is not absorbed at temperatures below 200° (392° F.), but at 350°—400° (662°—752° F.) absorption takes place slowly with formation of the compound KH_2. As, however, this body absorbs hydrogen in quantities varying with the pressure and temperature, it is necessary, in order to obtain it in a pure state, to remove the gas evolved on heating, until the pressure remains constant at that which corresponds with the tension of dissociation of the substance for that particular temperature. Potassic hydride is very brittle at the ordinary temperature, and has a metallic lustre and crystalline appearance resembling that of the amalgam of silver. It can be melted in an atmosphere of hydrogen without undergoing alteration. In a vacuum it begins to decompose at 200° (392° F.), and at 411° (771°·8 F.) the tension of the hydrogen evolved is $760^{mm.}$ (Troost and Hautefeuille, *Compt. Rend.*, 1874, lxxviii. 807).

(590) **POTASSIC CHLORIDE**, or *Chloride of potassium*; KCl = 74·6; *Density*, 1·994; *Comp. in* 100 *parts*; K, 52·41; Cl, 47·59.—This salt is extracted in considerable quantity from *kelp*, the ashes of burnt sea-weed, and from 'bittern,' the mother liquors from the evaporation of sea water (616), by a process invented by Balard: it is used largely as a source of the potassic salt required in the manufacture of alum. It may be prepared pure by directly neutralizing either the acid or the normal potassic carbonate with hydrochloric acid and evaporating. It crystallizes in cubes, and is very readily soluble in cold water, which

takes up about a third of its weight, attended with great depression of temperature. It is remarkable that this salt possesses the property of absorbing the vapours of sulphuric anhydride, forming a hard translucent mass, $KCl.SO_3$, which is instantly decomposed by water. With chromic acid it forms a corresponding compound, $KCl.CrO_3$, which is also decomposed by water: it is obtained in needles when a solution of potassic dichromate in hydrochloric acid is allowed to crystallize.

According to Bunsen, a blue subchloride of potassium also exists.

A native compound of chloride of potassium and magnesium is found in a bed of clay in the neighbourhood of Stassfurt, near Magdeburg, where it is immediately above a bed of rock-salt 100 feet or 30 metres in thickness. This is precisely the position which it would occupy, supposing the deposit to have been formed by the gradual drying up of an inland sea, where the common salt would crystallize out first, and the salts of magnesium and potassium afterwards. This bed of clay contains the sulphates and chlorides of potassium, of sodium, and of magnesium, and the upper part of the deposit consists chiefly of a hydrated double chloride of magnesium and potassium, $KCl.MgCl_2.6OH_2$, which has received the name of *carnallite*, from its pink colour, resembling rock-salt in appearance, but with a more pearly lustre, and extremely deliquescent. It is now extensively worked for the sake of the potassic chloride it contains, amounting to nearly one-fourth of its weight. At Kalusz, in the Eastern Carpathians, there is an extensive bed of *sylvin*, or native potassic chloride, which in some parts forms layers 2 to 3 feet thick of the almost chemically pure salt.

(591) **POTASSIC BROMIDE**, or *Bromide of potassium*; $KBr = 119{\cdot}1$; *Density*, 2·672; *Comp. in* 100 *parts*, K, 32·83; Br, 67·17.—This is a very soluble salt, crystallizing in cubes, which are sometimes elongated into prisms or flattened into plates. It may be obtained by adding bromine to a solution of potassic hydrate until the liquid permanently acquires a slight yellow colour: potassic bromide and bromate are formed. Löwig dissolves the mixed salts in water, decomposes the bromate by a current of sulphuretted hydrogen, warms gently to expel the excess of the gas, filters from the deposited sulphur, and evaporates until the solution crystallizes; $2KBrO_3 + 6SH_2 = 2KBr + 6OH_2 + 3S_2$. Potassium bromide can be freed from any iodide that may be present, by boiling its solution with bromine water.

(592) **POTASSIC IODIDE**, or *Iodide of potassium*; KI= 166·1; *Density*, 3·056; *Comp. in* 100 *parts*, I, 76·46; K, 23·54. —This salt, so valuable in medicine, may be prepared in several ways. A simple method consists in adding iodine to a solution of potassic hydrate gently warmed, until it begins to assume a brown tint. Iodide and iodate of potassium are formed; $3I_2+6KHO=5KI+KIO_3+3OH_2$. By gentle ignition of the residue obtained on evaporation, the iodate is decomposed, and the remaining iodide fuses. The salt must not be strongly heated, as potassic iodide volatilizes at a red heat. The iodate may be decomposed by sulphuretted hydrogen in the manner above described for the preparation of the bromide, and also by boiling with iron turnings, but this does not answer well with concentrated solutions. According to Pellagri (*Gazzetta Chimica Italiana*, 1875, v. 423), the iodate is very easily reduced by the employment of a couple consisting of a plate of iron and one of copper united by a wire: a deposit of ferric oxide is formed, which increases for about two days, when the green ferroso-ferric oxide begins to make its appearance; this is a sign that the reduction is completed. A better plan is to digest 2 parts of iodine and 1 part of iron, in a stoppered vessel, with ten parts of water, the iron being purposely added in excess; under these circumstances ferrous iodide is formed by the direct union of the metal with the iodine: the solution is decanted, and a quantity of iodine equal to one-third of that which it already contains is added, whereby a mixture of ferrous and ferric iodides is produced. The liquid is then boiled, and a solution of potassic carbonate is added in small quantities so long as effervescence is produced and a precipitate occurs; $Fe_2I_6+FeI_2+4K_2CO_3=8KI+Fe_3O_4+4CO_2$; the solution is next filtered from the dense magnetic oxide of iron, and on evaporation it yields crystals of potassic iodide; the oxide of iron, however, obstinately retains a portion of the potassic iodide.

Potassic iodide crystallizes in anhydrous cubes, which are not deliquescent in dry air. It is very soluble in water, and to a smaller extent in alcohol; it has a cooling, bitterish taste. Its solution has the property of dissolving iodine, with which it forms a deep brown liquid.

Pure potassic iodide is completely soluble in six times its weight of alcohol (density, 0·83); it should not effervesce when moistened with hydrochloric acid (carbonate would be indicated by effervescence), neither should it turn brown; if potassic iodate were mixed with it, free iodine would be shown by the brown

colour developed on adding the acid. If the solution of the iodide be mixed with strong nitric acid, an immediate separation of iodine occurs; $2KI+4HNO_3=2KNO_3+2OH_2+2NO_2+I_2$. A mixture of potassic dichromate and sulphuric acid gives a similar result; $K_2Cr_2O_7+7H_2SO_4+6KI=Cr_23SO_4+4K_2SO_4+7OH_2+3I_2$.

(593) **POTASSIC FLUORIDE**, or *Fluoride of potassium* ($KF=58{\cdot}1$; *Density*, 2·454) is a very deliquescent salt obtained by neutralizing hydrofluoric acid with a solution of potassic hydrate. Its solution has an alkaline reaction and corrodes glass.

Potassic Hydric Fluoride, or *Fluoride of potassium and hydrogen* ($KHF_2=78{\cdot}1$) crystallizes in tubes or rectangular four-sided tables from a solution of potassic fluoride in hydrofluoric acid; it is a convenient source for obtaining anhydrous hydrofluoric acid (470).

(594) **POTASSIC SILICOFLUORIDE**; $2KF.SiF_4=220{\cdot}2$.—This salt is one of the most insoluble compounds of potassium; it falls as a transparent gelatinous precipitate whenever hydrofluosilicic acid is added to a salt of potassium; it dries to a white earthy-looking powder. Advantage is occasionally taken of its insolubility to separate potassium from some of its salts: in this way chloric acid is sometimes prepared from potassic chlorate.

(595) **OXIDES OF POTASSIUM.**—Potassium forms three well-defined compounds with oxygen; a basic oxide, which constitutes potash, and furnishes the salts of the alkali; and two other oxides which do not form corresponding salts with acids. The blue film which is formed upon the surface of the metal during its gradual oxidation in dry air, and was formerly supposed to be a suboxide, is really a mixture, or perhaps a molecular combination of potassic oxide and dioxide.

			K.	O.	
Potash, Dipotassic oxide	...	K_2O = 94·2 or	83·01	+ 16·99	= 100
Potassic dioxide ...	...	K_2O_2 = 110·2 „	70·96	+ 29·04	= 100
Potassic peroxide ...	...	K_2O_4 = 142·2 „	54·99	+ 45·01	= 100.

(596) **DIPOTASSIC DIOXIDE**, $K_2O_2=110{\cdot}2$.—Dry air or nitrous oxide passed over potassium at temperatures below 100° (212° F.) causes the metal to exfoliate, and ultimately crumble to a greenish powder mixed with blue and yellow lumps; the latter appear to consist of nearly pure dioxide, K_2O_2, whilst the blue lumps are molecular combinations of the monoxide and dioxide in varying proportions. Both the dioxide and the tetroxide, when fused, are orange-red, becoming nearly black as the temperature rises (Lupton, *Jour. Chem. Soc.*, 1876, ii. 565).

(597) **PEROXIDE OF POTASSIUM**, *Dipotassic tetroxide*; $K_2O_4=142{\cdot}2$ (Harcourt, *Jour. Chem. Soc.*, 1861, xiv. 267).—This substance is formed when potassium is heated gently in a current of dry air; the operation must be completed in a current of dry oxygen gas: if formed at a temperature of 280° (536° F.), it slowly cakes together, but below that temperature it furnishes a powder of a chrome-yellow colour. It absorbs moisture rapidly when exposed to the air, and is decomposed by water with evolution of oxygen and formation of a solution of the oxide, K_2O_2.

(598) **DIPOTASSIC OXIDE**, or *Potash*; $K_2O=94{\cdot}2$.—This compound can be prepared by allowing thin slices of metallic potassium to become oxidized in air perfectly free from moisture and carbonic anhydride; or by heating potassium with an equivalent quantity of the hydrate, when hydrogen is expelled and pure potassic oxide is formed, $2KHO+K_2=KKO+H_2$. It is white, very deliquescent, and caustic; when moistened with water the two substances combine with incandescence, and after it has thus become hydrated, no degree of heat is sufficient to expel the water. Anhydrous potassic oxide has not yet been fused, and remains white even when intensely heated. It is said to be volatilized at a high temperature.

(599) **POTASSIC HYDRATE**, or *Caustic Potash*; KHO= $56{\cdot}1$; *Density*, $2{\cdot}2$; *Comp. in* 100 *parts*, K_2O, $83{\cdot}96$; OH_2, $16{\cdot}04$, is prepared by dissolving potassic carbonate, of which the *pearlash* of commerce is an impure variety, in 10 or 12 times its weight of water, and adding to the boiling solution a quantity of caustic lime equal in weight to half the potassic carbonate used; the lime should be slaked, made into a thin paste with water, and added in small portions at a time, so that the liquid may be maintained at the boiling point: a crystalline calcic carbonate is precipitated, and potassic hydrate remains in solution; $K_2CO_3+CaH_2O_2$ giving $2KHO+CaCO_3$. After decantation from the precipitate, the liquid is evaporated rapidly in a clean iron or silver basin, until at a heat approaching redness, it flows without ebullition, like oil: it is then either cast into cylinders in a metallic mould, or is poured upon a cold stone slab, and allowed to solidify. The hydrate may also be obtained crystallized in acute rhombohedrons, $KHO.2OH_2$, from a hot concentrated aqueous solution. A much purer product may be obtained by decomposing pure potassic nitrate at a red heat by metallic copper, or still better by the deflagration of a mixture of the nitrate with iron, as when copper is used the product is apt to be contaminated with that metal; the fused mass obtained in this way is extracted with water, and the clear solution evaporated and the residue fused in the manner above described.

Potassic hydrate is one of the most indispensable reagents to the chemist. It is therefore necessary that he should be able readily to ascertain its purity, and if needful prepare it for himself: when required pure, crystallized hydric potassic carbonate (commonly known as bicarbonate, $KHCO_3$), may be decomposed in the manner above described, by means of lime obtained from

black marble. The impurities which occur most frequently in ordinary caustic potash are peroxide of potassium, and the carbonates, sulphates, chlorides, and silicates of calcium, aluminium, iron, and lead. If pure, potassic hydrate is perfectly soluble in water without effervescence: a dilute solution should give no precipitate with baryta-water, showing the absence of carbonates and sulphates, neither should it yield any precipitate with ammonic oxalate, showing the absence of calcic salts. After neutralizing it with nitric acid, argentic nitrate gives no precipitate, showing the absence of chlorine. Freedom from iron or metallic impurities is shown by the absence of any precipitate on the addition of hydric ammonic sulphide, NH_4HS. Caustic potash, when pure, is entirely soluble in alcohol, the impurities above mentioned remaining undissolved. Common potash is therefore often purified by dissolving it in alcohol and evaporating the solution in a silver vessel, ultimately raising the temperature until it undergoes igneous fusion; the alcohol is thus expelled, the melted hydrate is poured off upon a silver plate from the black crust which forms over its surface, and when cold it is broken up and placed in a well-closed bottle.

A dilute solution of pure potassic hydrate may be readily obtained by adding a hot solution of baric hydrate to a solution of potassic sulphate, until the liquid gives no further precipitate, either with baryta or with potassic sulphate; $K_2SO_4 + BaH_2O_2 = BaSO_4 + 2KHO$.

Potassic hydrate, after fusion, is a hard, greyish-white substance: it absorbs both moisture and carbonic anhydride rapidly from the air; it is soluble in about half its weight of water, with the development of considerable heat, and is likewise very soluble in alcohol. Caustic potash has a peculiar nauseous odour, and an acrid taste; it is a powerful cautery, and quickly destroys both animal and vegetable matters; for this reason its solution cannot be filtered except through pounded glass or sand, and is always best clarified by allowing the impurities to subside, and then decanting the clear liquid. The solution should be preserved in glass bottles into the composition of which no oxide of lead enters, as the solution gradually dissolves this oxide out of glass. It also attacks vessels even of green glass and of porcelain when heated in them.

The following tables give approximately the proportions of potassic oxide and potassic hydrate contained in 100 parts by weight of solutions of the alkali of various densities:

Strength of Solutions of Potassic Hydrate at 15° (59° F.) (Tünnermann).

Density.	K_2O in 100 parts.	Density.	K_2O in 100 parts.	Density.	K_2O in 100 parts.
1·3300	28·290	1·1979	18·671	1·0819	8·487
1·3131	27·158	1·1839	17·540	1·0703	7·355
1·2966	26·027	1·1702	16·408	1·0589	6·224
1·2805	24·895	1·1568	15·277	1·0478	5·002
1·2648	23·764	1·1437	14·145	1·0369	3·961
1·2493	22·632	1·1308	13·013	1·0260	2·829
1·2342	21·500	1·1182	11·882	1·0153	1·697
1·2268	20·935	1·1059	10·750	1·0050	0·566
1·2122	19·803	1·0938	9·619		

Density of Potassic Hydrate Solutions (Schiff).

Density.	KHO in 100 parts.	Density.	KHO in 100 parts.	Density.	KHO in 100 parts.
1·036	5	1·288	30	1·604	55
1·077	10	1·349	35	1·667	60
1·124	15	1·411	40	1·729	65
1·175	20	1·475	45	1·790	70
1·230	25	1·539	50		

The *Liquor Potassæ* of the Pharmacopœia contains nearly 6 per cent. of potassic hydrate, and has a density of 1·058. The concentrated solution used for organic analysis may be obtained by dissolving 1 part of the solid hydrate in 2 parts of water.

Water cannot be expelled from potassic hydrate, as at a high temperature it is wholly volatilized by the mere application of heat. Its chemical attractions are so powerful that few vessels are found capable of resisting its action; those which contain silica are decomposed by it, and platinum itself is oxidized when strongly heated in contact with it: gold and silver resist it better. Potassic hydrate decomposes the fixed oils, and converts them into soluble soaps: when fused with siliceous minerals it displaces the bases, and combines with the silica, forming potassic silicate. Potassic salts are extensively employed in the arts: for the manufacture of certain kinds of soap and glass they are indispensable; the nitrate enters largely into the manufacture of gunpowder; and others of its salts in greater or less quantity furnish important aids to a variety of processes employed in the manufactures of the country. In the laboratory potassic hydrate is in constant use for absorbing acid gases, such as carbonic acid, and for separating the metallic oxides from solutions of their salts, since owing to the powerful attraction of the alkali for acids, it

readily decomposes the salts of all the metals which produce oxides insoluble in water. Salts of potash also constitute in small proportion, a necessary article of food; as according to Liebig the prolonged withdrawal of these compounds is the chief cause of scurvy, so that they form a necessary constituent in antiscorbutic remedies.

Compounds of potassium are present in small proportion in all fertile soils, the grand reservoirs of this alkali-metal being the different varieties of clay, which contain 2 or 3 per cent. of it, derived from the disintegration of felspar, in which mineral it exists in the proportion of from 10 to 12 per cent., and certain kinds of mica, which yield 5 or 6 per cent.: besides these, numerous other silicates contain a small proportion of potash. By exposure to the air and atmospheric vicissitudes, these rocks become gradually disintegrated by the action of the carbonic acid in rain water, and among the soluble products of their decomposition potassic carbonate is assimilated by plants; they accumulate it especially in the leaves, young shoots, and succulent parts in the form of potassic salts, usually of organic acids. Owing to this circumstance large quantities of potash may be obtained with facility: dried brushwood is incinerated, and the remaining ash, which seldom constitutes more than 1 per cent. of the dry wood, contains the potassium in the form of carbonate: this salt is then extracted by water from the insoluble portions. M. Merle now obtains considerable quantities of potassic chloride from the mother-liquors of sea-water by a modification of the method of Balard (616). Much potash accumulates as an organic salt in the fleece of the sheep and is wasted. Maumené and Rogelet collected this peculiar potassic salt, which is called 'suint,' by simply washing, and evaporating the wash water. A fleece weighing 4 kilos., or 9 lb., contains about 7 ounces (200 grams) of pure potash, of which they consider nearly 6 oz. to be recoverable. A good deal of the potash which is carried off the land cultivated for beet-root is now recoverable by suitable treatment of the waste after the sugar has been extracted: this on being ignited leaves a black porous mass containing potassic and sodic carbonates and potassic chloride and sulphate. The black mass is extracted with water and the salts separated by careful fractional crystallization. In this way 'potash' containing more than 80 per cent. of carbonate may be obtained, whilst the potassic chloride and sulphate are separated in the pure state. The most important sources of potash salts, however, are the Stassfurt beds and those at Kalusz (p. 405).

Messrs. Ward and Wynants a few years ago contrived a method of extracting potash from felspar in the form of carbonated or of caustic alkali, but the process does not seem to have been commercially successful. The felspar is first ground to a fine powder, and mixed with a suitable quantity of chalk, slaked lime, and fluorspar; it is then fritted in a furnace, at a temperature somewhere about the softening point of silver, the mixture not being allowed actually to melt. The chalk during the ignition evolves carbonic anhydride, which mechanically preserves the porosity of the mass, and facilitates the extraction of the soluble products. The mass obtained is then lixiviated, and rendered caustic by the addition of slaked lime. The proportion of lime required is indicated by the following formulæ, supposing the materials to be employed in a pure state: $K_2O.3SiO_2.Al_2O_3.3SiO_2 + 7\frac{1}{2}CaO + CaF_2$.—(*Hoffmann's Jury Report*, 1862, p. 51.)

(600) **SULPHIDES OF POTASSIUM.**—Potassium takes fire readily and burns with brilliancy when heated in the vapour of sulphur. It combines with this element in not less than 4 and possibly in 5 different proportions, K_2S?, K_2S_2, K_2S_3, K_2S_4, and K_2S_5. Owing to this circumstance, the reactions which occur when sulphur is heated with potassic hydrate or carbonate are somewhat complicated, but as they are well understood, they may be traced without difficulty.

Dipotassic Sulphide, or *Protosulphide of potassium*; K_2S.—Some doubt exists as to the possibility of forming this compound. The usual directions are to heat potassic sulphate in a current of dry hydrogen, or to mix the sulphate intimately with finely powdered charcoal, and ignite it in covered vessels. Bauer, however (*Chem. Gaz.*, 1858, 468), finds that the result is not that usually represented by the equation, $K_2SO_4 + 4H_2 = K_2S + 4OH_2$, but that a mixture of free alkali and a variable amount of one of the higher sulphides of potassium is the result. The residue obtained has a reddish-yellow colour; it is deliquescent, and acts powerfully upon the skin as a caustic. When sulphuretted hydrogen is passed through a solution of potassic hydrate, it is rapidly absorbed, and if the current of gas be continued until the liquid is completely saturated, the compound KHS will be formed: on evaporating this solution in vacuo colourless transparent rhombohedrons of hydrated *potassic hydric sulphide* or *potassic thiohydrate*, $2KHS.OH_2$, are obtained which give off their water of crystallization at about 200° (392° F.), and melt at a dull redheat to a mobile yellow liquid. The solution of this sulphide is colour-

less when first prepared, but if exposed to the air it quickly absorbs oxygen, and acquires a yellow colour, owing to the formation of the sulphide K_2S_2; $4KHS + O_2 = 2K_2S_2 + 2OH_2$. If a solution of potash be divided into two equal portions and one be converted into the hydric potassic sulphide, KHS, and be then mixed with the other half of the solution of potash, a solution of pure dipotassic sulphide will be obtained, $KHS + KHO$ becoming $K_2S + OH_2$; on evaporating this solution in a vacuum, deliquescent four-sided prisms are obtained having a composition represented by the formula $K_2S.5OH_2$: at 150° (302° F.) they lose water and leave the hydrate, $K_2S.2OH_2$. On the addition of a strong acid to the solution, sulphuretted hydrogen is given off abundantly, no sulphur being deposited; $K_2S + H_2SO_4 = SH_2 + K_2SO_4$.

If potassic sulphate be mixed in fine powder with half its weight of lampblack, and heated in a covered crucible, the sulphate is reduced leaving an impure sulphide, which remains in a finely divided state mixed with the excess of charcoal, and yields a *pyrophorus*, or compound which takes fire spontaneously on exposure to the air, owing to the heat developed by its rapid absorption of oxygen.

The *Bisulphide*, or *Dipotassic bisulphide*, K_2S_2, may be formed by exposing an alcoholic solution of KHS to the air until it begins to become turbid, and evaporating to dryness *in vacuo*. It fuses easily, and is of an orange colour.

The *Sesquisulphide* (*tersulphide* formerly), K_2S_3, is obtained pure by passing the vapour of carbonic bisulphide over ignited potassic carbonate as long as any gas makes its escape: carbonic anhydride and carbonic oxide are produced, as follows: $2K_2CO_3 + 3CS_2 = 2K_2S_3 + 4CO + CO_2$. In the old process of making *liver of sulphur*, 69 parts of dry pearlash are fused with 40 parts of sulphur; the resulting yellowish-brown mass consists of 3 molecules of sesquisulphide and 1 molecule of potassic sulphate: part of the carbonate in this case yields oxygen to one portion of the sulphur, and forms sulphuric acid, whilst the remainder is converted into the sulphide, as shown in the annexed equation: $4K_2CO_3 + 5S_2 = K_2SO_4 + 3K_2S_3 + 4CO_2$.

A *Dipotassic tetrasulphide*, K_2S_4 or K_2SS_3, corresponding to the sulphite, K_2SO_3, was supposed to be formed by reducing potassic sulphate by the vapour of carbonic bisulphide, but from Schöne's experiments it would appear to be a mixture approximating in composition to K_4S_7, it may, however, be prepared in the wet way by dissolving the proper quantity of sulphur in an aqueous solution of the monosulphide and evaporating the solution *in vacuo*; by this means thin orange-red hygroscopic laminæ are obtained containing $K_2S_4.2OH_2$.

Dipotassic pentasulphide, or *persulphide*, K_2S_5 or K_2SS_4, corresponding to the sulphate, K_2SO_4, is formed by boiling a solution of any of the preceding sulphides with excess of sulphur until saturated: or by fusing any of the dry sulphides with an excess of sulphur; the excess of sulphur separates and floats above the sulphide, which has a dark liver-brown colour; it is deliquescent, and forms a deep yellow solution in water.

All these sulphides give an alkaline reaction with test-paper, and an odour of sulphuretted hydrogen more or less distinct. On the addition of a stronger acid they are decomposed with

evolution of sulphuretted hydrogen, attended in the case of all but the lowest sulphide, by the precipitation of white, finely divided sulphur. On adding the persulphide to an excess of hydrochloric acid of density about 1·1, the persulphide of hydrogen (417) is separated as an oily liquid. By exposing solutions of the higher sulphides to air, they become colourless, potassic thiosulphate is formed, and the excess of sulphur is separated. When a solution of potassic hydrate is boiled with sulphur, a decomposition ensues similar to that which occurs when the two compounds are fused together; a deep reddish-yellow liquid is formed, which contains the thiosulphate, and one of the higher sulphides of the metal: 6 molecules of potassic hydrate and 12 atoms of sulphur would thus furnish 1 molecule of thiosulphate and 2 of persulphide of potassium; $6KHO+6S_2=K_2S_2O_3+2K_2S_5+3OH_2$.

(601) **POTASSIC SULPHATE**, or *Sulphate of potassium*; $K_2SO_4=174·2$; *Density*, 2·66; *Comp. in* 100 *parts*, K_2O, 54·07; SO_3, 45·93.—This salt crystallizes either in anhydrous six-sided prisms, terminating in six-sided pyramids, or in four-sided oblique rhombic prisms; it requires about 12 parts of water at 0° (32° F.) for its solution. The crystals decrepitate strongly when heated. Potassic sulphate forms a series of double salts with the sulphates of the metals isomorphous with magnesium, and another class of salts (the alums) with the sulphates of the metals isomorphous with aluminium. Jacquelain finds that if normal potassic sulphate be dissolved in nitric acid, a little nitre and hydric potassic sulphate, $KHSO_4$, are formed, whilst a salt consisting of $HNO_3.K_2SO_4$ crystallizes out in oblique prisms. An analogous compound, $H_3PO_4.K_2SO_4$, may be formed with phosphoric acid.

(602) **HYDRIC POTASSIC SULPHATE**, *Acid sulphate*, or *Bisulphate of potassium*; $KHSO_4=136·1$; *Density*, 2·475.—This salt is formed on a large scale as a residuary product in the preparation of nitric acid from potassic nitrate. A large quantity of potassic sulphate is obtained from the beds of *kainite* at Kalusz: this mineral consists of potassic and magnesic sulphates with magnesic and sodic chlorides: kainite also occurs at Stassfurt. It crystallizes from a strongly acid solution in rhomboidal tables, which fuse at a heat below redness and give off the elements of water, leaving a compound of the formula $K_2S_2O_7$ or $K_2SO_4.SO_3$, which, by prolonged ignition, loses SO_3 and leaves the normal sulphate. The crystals of the hydric sulphate are very soluble in water and have a sour bitterish taste, but if redissolved in water, the normal sulphate crystallizes first, and afterwards, when the

liquid has become strongly acid, the bisulphate is deposited. This salt is sometimes used as a flux in cases where the action of an acid is required at a high temperature upon salts or metallic oxides with which it may be fused. The compound, $K_2S_2O_7$, *dipotassic pyrosulphate*, the normal potassic salt of pyrosulphuric acid (p. 217) above mentioned, may also be prepared by heating the sulphate, K_2SO_4, with sulphuric anhydride. It crystallizes in needles, and when dissolved in hot fuming sulphuric acid, the solution as it cools deposits hydric potassic pyrosulphate, KHS_2O_7, in transparent prisms which melt at 168° (334°·4 F.) According to Lescœur (*Compt. Rend.*, 1874, lxxviii. 1044), a 'quadrisulphate,' $K_2SO_4.3SO_3.6OH_2$, is deposited from a hot solution of potassic sulphate in sulphuric acid, in large flexible nacreous plates which melt at 61° (141°·8 F.).

(603) **POTASSIC NITRATE**, or *Nitrate of potassium*; $KNO_3 = 101·1$; *Density*, 2·070; *Comp. in* 100 *parts*, K_2O, 46·59; N_2O_5, 53·41.—*Saltpetre*, or *Nitre* as this salt is frequently termed, is one of the most important and valuable salts of potassium. The principal supply of nitre is derived from various districts in the East Indies, where it occurs sometimes as an efflorescence upon the soil, at other times disseminated through the superficial stratum itself. It appears to be formed in the moist portions of the soil, at some little distance below the surface, towards which it is raised by capillary action. The nitre is obtained by lixiviating the soil, and allowing the solution to crystallize. The earth which furnishes it consists principally of loose porous calcic carbonate, mixed with decomposing felspar, and it always contains more or less of organic matters. In temperate climates, either nitrites or nitrates are almost always found in the shallow well-waters of towns, owing to the oxidation of nitrogen contained in the animal *débris* during their infiltration through the soil. Notwithstanding the numerous investigations of which it has been the subject, including in later times those of J. Davy, of Kuhlmann, of Schönbein, and others, the process of nitrification is still very imperfectly understood. The artificial formation of nitre has, however, been practised with considerable success in various countries of Europe, furnishing annually a large amount of the salt. In Sweden this supply of nitre is considered of such importance that each landed proprietor is obliged to pay a certain tax in raw nitre, the quantity required being proportioned to the value of the estate.

Where animal matters are present in abundance, the formation of nitric acid is chiefly due to the gradual oxidation of

ammonia developed in the process of putrefaction. The free access of air and the presence of a certain amount of moisture is necessary; the oxidation is also materially favoured by an excess of an alkaline or earthy carbonate, or of some basic substance which can combine with the acid at the moment of its generation, and also, it would seem, of hydrated ferric oxide, since Pesci found (*Gaz. Chim. Ital.*, 1876, vi. 307) that the oxide is capable of rapidly converting ammonia into nitrates and nitrites, and that, even when oxygen is excluded, the ferric oxide being partially reduced under these circumstances. It is from this cause, no doubt, that an ocherous chalk is preferred in forming a nitre plantation. Ozone appears to have the power of combining directly with nitrogen; and Schönbein conjectures that it may be concerned in the natural production of nitric acid, so that nitrification is, in favourable cases, due to the slow combination of atmospheric nitrogen and oxygen. Boussingault's experiments, however, render this improbable, and it would seem rather that the nitrates are produced by the oxidation of ammonia. The process of nitrification becomes arrested if the temperature be allowed to fall much below 15° (59° F.).

Nitre Plantations.—The method adopted for the artificial production of nitre consists in placing animal matters, mingled with ashes and lime rubbish, in loosely aggregated heaps, exposed to the air, but sheltered from rain. These heaps are watered from time to time with urine or stable runnings, the heap being kept damp, but not wet; at suitable intervals the earth is lixiviated, and the salt crystallized. Three years usually elapse before the nitre bed is washed: after this interval a cubic foot of the *débris* should yield between 4 and 5 ounces of nitre, or a cubic metre, about 4 kilos. As there is always a considerable quantity of calcic and magnesic nitrates present, which will not crystallize, potassic carbonate, in the shape of wood ashes, is added so long as any precipitate occurs. By this means the calcic nitrate is decomposed, and the insoluble calcic carbonate separated; $K_2CO_3 + Ca2NO_3 = CaCO_3 + 2KNO_3$. The clear liquor is then evaporated and crystallized. It is found by the saltpetre-boiler that the earth in which nitre has once been formed furnishes fresh nitre more readily than on the first occasion. Care is taken that the *nitre plantations*, as they are termed, shall rest upon an impervious flooring of clay, so that the liquid which drains away from them may be collected and preserved.

In Prussia, by a more methodical treatment, a cubic metre of the earth yields about 20 kilos. of nitre. The heaps are so con-

structed as to form a terrace of steps, exposing the back in the form of an upright wall to the prevailing wind; the watering is thus facilitated, whilst the evaporation proceeds with rapidity upon the exposed side, where, from capillary action, the nitre chiefly accumulates: from time to time a layer of earth is removed from this wall for lixiviation, and the washed earth, mixed with a fresh portion of animal matter, is returned systematically to the other side of the heap. The washing of the earth charged with saltpetre is conducted in a systematic manner (627), so as to avoid using a larger quantity of water than is actually needed to dissolve the saltpetre.

Besides the natural and artificial sources of nitre just described, this salt occurs also in solution in the sap of certain plants, among which the sunflower, the tobacco plant, and common borage may be enumerated.

Properties.—Nitre usually crystallizes in long six-sided striated prisms, terminated by dihedral summits; but it is a dimorphous salt, and is occasionally obtained by spontaneous evaporation of small drops of its solution in microscopic rhombohedra, isomorphous with those of sodic nitrate: it is soluble in $3\frac{1}{2}$ times its weight of water at 18° (64°·4 F.), and in about a third of its weight of boiling water; it is insoluble in alcohol: its taste is cooling and saline. If paper be dipped in a solution of nitre and dried, it forms the well-known *touch-paper*, which, when ignited, steadily smoulders away until it is consumed, and on this account is largely employed in firing trains of powder, fireworks, &c. Nitre fuses easily without decomposition at a temperature of 358° (676°·4 F.), and when cast into moulds, solidifies to a white, fibrous, translucent, radiated mass, known as *sal prunelle*. When heated to redness, part of its oxygen is expelled, and a deliquescent mass of impure potassic nitrite is formed. By a still stronger heat the nitrite is decomposed, nitrogen mixed with oxygen escapes, and a mixture of potassic oxide and peroxide remains.

Owing to the facility with which nitre parts with oxygen, it is a powerful oxidizing agent, and is frequently used in the laboratory as such: when thrown upon glowing coals it produces a brisk scintillation. If nitre be intimately mixed with any metallic sulphide in fine powder, such as antimonious sulphide, and thrown, in small quantities at a time, into a red-hot crucible, the sulphur burns with a brisk *deflagration*, or rapid combustion, at the expense of the oxygen of the nitre, and forms potassic sulphate with a portion of its potassium, whilst the metal at the

same time becomes oxidized to the maximum. In the case of antimony, the oxide produced possesses acid characters, and also forms a compound with the potassium. Baumé's quick flux consists of a mixture of 3 parts of nitre, 1 part of sulphur, and 1 of sawdust; the heat given out during its combustion is so great, that if a small silver coin be put into a mass of the mixture which will go into a walnut-shell, and it be kindled, the coin will be melted. Advantage is sometimes taken of the oxidizing action of nitre, in order to convert into sulphuric acid the small quantities of sulphur existing in certain substances of organic origin, for the purpose of estimating the proportion of sulphur which they contain. The quantity of sulphuric acid thus produced is precipitated and weighed as baric sulphate.

(604) **Refining of Saltpetre.**—The impurities of most frequent occurrence in nitre are potassic and sodic sulphates and chlorides, and calcic and magnesic nitrates: after it has been fused, unless the heat has been cautiously regulated, a little potassic nitrite is liable to be formed: in the latter case a fragment of the salt, when moistened with solution of cupric sulphate, becomes of a bright green colour. Nitre may be quickly deprived of chlorine by moistening the finely-powdered salt with pure nitric acid, and gently heating it until a portion of it, when dissolved in water, gives no precipitate with argentic nitrate. Nitre, when pure, is not deliquescent, and its solution gives no precipitate with solutions of baric chloride, argentic nitrate, or potassic carbonate.

In the refining of nitre, advantage is taken of the circumstance that whilst the solubility of nitre increases rapidly as the temperature rises, that of sodic chloride is scarcely affected by it. It was formerly the practice to purify the salt by three successive crystallizations; but the same object is now effected by a single operation, in the following manner:—In a deep copper boiler, 600 litres, or about 100 gallons of water is placed, and twice its weight of crude nitre is added: this salt gradually becomes dissolved, and fresh nitre is added, until, when the water has attained the boiling-point, a quantity of nitre has been added equal to three times the weight of the water employed;* when the liquid has been rendered clear by a few minutes' ebullition, it is strained through bag filters, and allowed to run into the crystallizing pan.

The crystallization is effected in a shallow vessel, the bottom of which is formed by two inclined planes which meet in the middle. In this vessel the solution is kept in continual agitation, in order to prevent the formation of large

* The quantity of sodic chloride in *grough* or crude East Indian nitre is generally small; but in the artificial nitre obtained from the 'beds' it often rises to a large amount: in such a case the liquid is skimmed from time to time, and the sodic chloride, a large proportion of which remains undissolved, is removed by means of perforated ladles; as soon as nitre equal to about 5 times the weight of the water has been added, the solution is diluted with two-thirds the quantity of water at first employed, after which, if the liquid be strongly coloured, 1 kilogram (about 2¼ lbs.) of glue, dissolved in hot water, is added, and thoroughly incorporated by briskly stirring; the coagulum which is formed rises in a scum to the surface, collecting the greater part of the organic impurities derived from the nitre heap; this is carefully removed, and the operation is afterwards continued as above described.

crystals; such crystals would mechanically retain the mother-liquor, from which they could not be subsequently freed without recrystallization. The sodic chloride, being nearly as soluble in cold water as in hot, remains almost entirely in the solution, whilst the saltpetre is deposited in extremely small crystals, technically termed *saltpetre flour;* these are allowed to drain, and are then removed to tanks provided with false perforated bottoms, where they are deprived of the mother-liquor with which they are saturated. For this purpose, the tanks are completely filled with the crystals, and upon them is poured a solution of saltpetre saturated in the cold; this liquid dissolves the chlorides, but leaves the pure nitre undissolved. In the course of a few hours, the liquid is drawn off, and the tanks are then filled up with pure water; this becomes charged with nitre containing traces of chlorides, whilst the undissolved salt is almost chemically pure: the solution of nitre thus obtained serves to wash a fresh portion of the crystals; after the last portions of mother-liquor have been removed by the centrifugal machine, the refined saltpetre is dried, and is then fit for use.

Very large quantities of potassic nitrate are now manufactured from the sodic nitrate which is found in South America in the district lying on the frontier of Peru and Chili. The sodic nitrate is mixed with an equivalent quantity of potassic chloride and dissolved in the requisite quantity of water in large iron tanks by blowing in steam. The clear solution is then drawn off and allowed to cool with constant agitation, so that the potassic nitrate may be deposited in very small crystals, which are drained and purified in the same manner as 'saltpetre flour,' whilst the sodic chloride formed remains in the mother-liquor. This mother-liquor, however, still contains potassic nitrate, besides the large quantity of sodic chloride: to separate these the solution is boiled down, and the common salt which is deposited in the boiling liquor is removed by perforated ladles. The clear solution on cooling then deposits a further quantity of potassic nitrate. In Belgium, potassic carbonate from the residues of the beet-root sugar manufacture is employed for decomposing the sodic nitrate instead of potassic chloride.

(605) **GUNPOWDER.**—The principal consumption of nitre is in the manufacture of gunpowder, which consists of an intimate mechanical mixture of nitre, sulphur, and charcoal, in proportions approaching to 1 atom of sulphur, 2 molecules of nitre, and 3 atoms of charcoal:

						In 100 parts.
Nitre	...	$2KNO_3$	=	202	...	74·8
Sulphur	...	S	=	32	...	11·9
Charcoal	...	3C	=	36	...	13·3
				270		100·0

The proportions used vary a little in different countries, as will be seen from the following table:

Composition of Gunpowder in 100 *parts.*

	English and Austrian.	Prussian.	Swedish.	Chinese.	French.		
Nitre ...	75	75·0	75	75·7	75·0	76·9	62
Sulphur	10	11·5	9	9·9	12·5	9·6	20
Charcoal	15	13·5	16	14·4	12·5	13·5	18
	Musket.	Musket.	Musket.		Musket.	Sporting.	Blasting.

An excess of sulphur is carefully avoided, on account of its injurious action upon the metal of the gun. The powder usually contains from ·8 to 1·5 per cent. of hydroscopic moisture.

The great explosive power of gunpowder is due to the sudden development of a large volume of gaseous bodies, consisting chiefly of nitrogen and carbonic anhydride, which, at the ordinary temperature of the air, would occupy a space equal to about 300 times the bulk of the powder used: but from the intense heat developed at the moment of the explosion, the dilatation amounts to at least 1500 times the volume of the gunpowder employed. Supposing the mixture to be made in the proportion of 1 atom of sulphur, 2 molecules of nitre, and 3 atoms of carbon, the reaction is often approximatively represented thus:

$$S_2 + 6C + 4KNO_3 = 6CO_2 + 2N_2 + 2K_2S.$$

The actual results, however, cannot readily be represented by any simple formula, and the solid residue, instead of consisting chiefly of potassic disulphide, contains but a small quantity of this substance, whilst potassic sulphate and carbonate are found in abundance, as also small quantities of potassic thiosulphate and ammonic 'sesquicarbonate'; some sulphur and charcoal also escape oxidation. These solid compounds in a finely divided state constitute the white smoke observed when gunpowder is fired.* Noble and Abel have recently examined the products of the explosion of gunpowder in a confined space with the greatest care, and they find that besides the solid compounds just mentioned, traces of potassic sulphocyanate are invariably produced, and that some of the nitrate always escapes decomposition. The results of their experiments show that the chemical theory of the decomposition of gunpowder based on the results of Bunsen and Schischkoff, is as far from representing the facts as the equation given above.

* In burning gunpowder in a copper tube with the view of collecting the gases over mercury, Chevreul found a small proportion of nitric oxide, of carbonic oxide, and of carburetted hydrogen, with a little sulphuretted hydrogen, mixed with the nitrogen and carbonic anhydride. Bunsen, and Linck, obtained results somewhat different, but the temperature, and consequently also the results of the combustion procured by this regulated action, are different from those attending the firing of ordnance. Karolyi, however (*Phil. Mag.*, Oct. 1863), succeeded in analysing the gases of gunpowder which have been fired in conditions closely resembling those which occur in artillery practice. For this purpose he enclosed a charge of powder in an iron cylinder of such strength that it just burst when the powder was fired by means of the electric spark. This charged cylinder was suspended in a hollow spherical bomb, from which the air was exhausted before firing. After the explosion had been produced, the gases and

Much care is requisite in the selection of the materials for the manufacture of gunpowder. The charcoal must be burned thoroughly, but not at too high a

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the solid residue of the powder were submitted to analysis. The results obtained were the following:

1. *Composition of the powder used.*

	Ordnance powder.		Small-arms powder.		Pebble powder. (Noble and Abel.)	
Nitre	73·78		77·15		74·67	
Sulphur	12·80		8·63		10·07	
Charcoal. Carbon	10·88		11·78		12·12	
Hydrogen ...	0·38	13·39	0·42	14·27	0·42	14·22
Oxygen	1·82		1·79		1·45	
Ash	0·31		0·28		0·23	
Water	—		—		0·95	
	99·97		100·05		99·91	

2. *Products of Combustion of* 100 *parts by weight.*

Nitrogen	9·77	10·06	11·39
Carbonic anhydride ...	17·39	21·79	27·70
Carbonic oxide ...	2·64	1·47	4·73
Hydrogen	0·11	0·14	0·05
Sulph. hydrogen ...	0·27	0·23	0·84
Marsh gas	0·40	0·49	0·12
Total gaseous ...	30·58	34·18	44 83
Ammonic sesquicarbonate	2·68	2·66	0·04
Potassic sulphate ...	36·95	36·17	6·58
„ carbonate ...	19·40	20·78	30·98
„ thiosulphate ...	2·85	1·77	3·38
„ sulphide ...	0·11	0·00	10·55
Charcoal	2·57	2·60	—
Sulphur	4·69	1·16	3·40
Loss	0·17	0·68	—
Potassic sulphocyanate	—	—	0·13
„ nitrate ...	—	—	0·11
Total solid ...	69·42	65·82	55·17

3. *Products of Combustion by volume in* 100 *of Gas.*

Nitrogen	37·58	35·33	32·19
Carbonic anhydride ...	42·74	48·90	49·82
Carbonic oxide ...	10·19	5·18	13·36
Hydrogen	5·93	6·90	2·08
Sulphuretted hydrogen	0·86	0·67	1·96
Marsh gas	2·70	3·02	0·58
	100·00	100·00	99.99

These gases contained a sufficient amount of carbonic oxide, and of hydrogen and

temperature: that from the willow, alder, or dogwood is preferred for the purpose, dogwood charcoal being employed only in making rifle powder. The charcoal always contains a notable proportion of hydrogen and oxygen. In the Government works at Waltham Abbey, sulphur is never used in the state of flowers of sulphur; in this condition it is preferred for fireworks; but distilled sulphur, reduced to a fine meal by grinding, is always used for gunpowder. The flowers of sulphur always contain sulphurous acid, which becomes speedily converted into sulphuric acid and attracts moisture. Nitre of the purest quality is alone employed. These three materials having been separately ground and sifted, are mixed in powder in the proper proportions, and are intimately blended in a revolving drum; they are then made into a stiff paste with water, and ground for some hours under edge-stones in the *incorporating-mill;* the slightly coherent mass thus procured is broken up, and spread, in layers of about an inch in thickness, between plates of gun-metal; it is then subjected to the action of a hydraulic press which exerts a force of 70 tons upon the square foot: a hard sonorous mass, termed *press cake,* is thus obtained; these masses, whilst still damp, are broken into small fragments, or *granulated,* by submitting them to the action of toothed rollers in a machine constructed for the purpose. The grains are next sorted by means of sieves into different sizes, after which they are thoroughly dried in closets heated by steam, and, finally, are *glazed,* or polished by placing them in barrels caused to revolve about 39 times in a minute. Mining powder is often glazed by adding powdered graphite in the polishing barrels; this operation retards the rate of ignition, and diminishes the hygroscopic character of the powder. A cubic foot of good English cannon powder weighs about 58 lb.; if below 55 lb., it is considered unfit for use. The heavier the powder the greater is its explosive power. Two ounces of the best English powder, when introduced into a mortar of 8 inches diameter, set at an angle of 45°, should throw a 68 lb. shot from 260 to 280 feet, on level ground.

Good gunpowder burns rapidly in the open air, leaving little residue, not blackening or kindling paper upon which it is fired. It has been found that a powerful concussion of powder between two pieces of iron will frequently kindle it, and if the powder be placed upon lead, or even upon a board, it may be exploded by the blow of a leaden bullet fired at it. The temperature at which it takes fire is about 250° (482° F.).

The object of granulating the powder, independently of the diminution of its tendency to absorb moisture, is to favour the rapidity of inflammation, by leaving interstices through which the flame is enabled to penetrate and envelope each grain. The ignition of the whole charge does not take place simultaneously

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its compounds, to take fire on the application of a lighted match. The formation of ammonic sesquicarbonate and of potassic carbonate in such large proportion is remarkable. The results obtained by the analysis of sporting powder by Bunsen and Schischkoff (*Pog. Ann.*, 1857, cii 321) do not materially differ from those quoted above; but are slightly modified by the excess of nitre used in the preparation of this kind of powder. Noble and Abel have also quite recently determined the amount of the various solid and gaseous products formed by the explosion of various kinds of gunpowder, as also the pressure exerted when it is fired in a closed space, and in the bore of a gun.

throughout, nor is it desirable that it should do so, otherwise sufficient time would not be given to allow the ball to receive the full advantage of the expansive force of the gas generated; too rapid an action would be expended upon the barrel of the gun itself, and effects would be produced like those due to fulminating mercury. This is especially the case with the very heavy ordnance now in use, and in order to overcome the difficulty a particular kind of powder, termed 'pebble powder,' is used, consisting of blocks or cubes often measuring as much as 1·75 inches on the side, only differing from the ordinary cannon powder in the size of the grains. Where a prolonged heaving force is required, as in blasting for mining operations, the action of the powder is still further retarded by mixing it with sawdust; the powder employed for this purpose usually contains 65 parts of nitre, 20 of sulphur, and 15 of charcoal; in many cases, however, small charges of 'dynamite,' a nitroglycerin compound, may be substituted for blasting powder with advantage. In the formation of the fusee, the quick and slow match, and certain kinds of fireworks, gunpowder is mingled with combustibles in various proportions.

The analysis of gunpowder is easily effected: 100 grains of the powder for examination are dried over sulphuric acid *in vacuo*; the loss indicates the amount of moisture. The residue is digested in water, and washed; the solution, when evaporated in a counterpoised capsule, and weighed, furnishes the amount of nitre and other salts. Baric nitrate, when added to a solution of these salts, acidulated with nitric acid, will yield the sulphuric acid in the form of baric sulphate; and argentic nitrate, when added to the liquid filtered from the baric sulphate, will give the data for ascertaining the amount of chlorine from the precipitated argentic chloride. The charcoal and sulphur are contained in the portion which does not dissolve in water; they may be separated by means of carbonic bisulphide or by the use of benzene at a boiling temperature, which dissolves out the sulphur, and leaves it in the crystalline form by spontaneous evaporation, whilst the charcoal is left undissolved and may be weighed.

A mixture of 3 parts of nitre, 2 of potassic carbonate, and 1 part of sulphur, produces a substance known as *pulvis fulminans*, which when heated on an iron shovel until fusion takes place, explodes suddenly with a very loud report.

(606) **POTASSIC NITRITE**, or *Nitrite of potassium*, KNO_2, is a white anhydrous, deliquescent salt, which may be obtained in crystals. It may be prepared by decomposing nitre by fusion at a red heat, dissolving the residue in water, and allowing the nitre to crystallize out. By careful crystallization almost the whole of the nitrate may be removed, leaving a concentrated solution of the nitrite, which may be obtained in the solid state by evaporating to dryness. Etard (*Compt. Rend.*, 1877, lxxxiv. 234) recommends the fusion of equal molecular weights of potassic nitrate and sulphite at a red heat, whereby the sulphite is oxidized to sulphate, and the nitrate reduced to nitrite. The latter may be

extracted by treating the powdered product with alcohol. It forms numerous double salts with other metallic nitrites (406).

(607) **POTASSIC CHLORATE**, or *Chlorate of potassium*; $KClO_3 = 122{\cdot}6$; *Density*, 2·326; *Comp. in* 100 *parts*, K_2O, 38·42, and Cl_2O_5, 61·58.—One mode of preparing this salt has already been explained (360). It may be more economically obtained by converting milk of lime into a mixture of calcic chlorate and chloride by passing through it an excess of chlorine; to a concentrated solution of the mixed salts, potassic chloride is then added in the proportion of 74·5 parts of the chloride to 168 parts of the caustic lime originally employed. In the process now generally employed for preparing the salt on a large scale, excess of chlorine is passed into a mixture of 300 parts of lime and 154 of potassic chloride with a comparatively small quantity of water, the operation being performed in close leaden tanks provided with agitators and heated by steam. The calcic chlorate and potassic chloride decompose each other, and potassic chlorate and calcic chloride are formed, $Ca2ClO_3 + 2KCl = 2KClO_3 + CaCl_2$; boiling water dissolves both the potassic chlorate and the calcic chloride. The two salts are easily separated by crystallization, as the potassic chlorate requires 16 parts of cold water for solution, whilst the calcic chloride is excessively soluble. From this mixture the chlorate is deposited in 6-sided prisms, which after recrystallization from boiling water form anhydrous 6-sided plates; it has a cooling taste, somewhat analogous to that of nitre: 100 parts of boiling water dissolve 61·5 of the salt. When heated it melts at about 370° (698° F.), and at 400° (752° F.) begins to be decomposed, furnishing oxygen gas of great purity, and leaving potassic chloride and perchlorate as a fixed residue behind. When heated to redness, it is entirely decomposed, 100 parts of the salt leaving 60·85 parts of potassic chloride, whilst 39·15 of oxygen are evolved. The chlorate is a more powerful oxidizing agent than nitre; and if combustible substances, such as sulphur or phosphorus, be rubbed with it forcibly, the combination of the combustible with oxygen ensues, accompanied by detonation. It is rapidly reduced when its aqueous solution is agitated with iron filings, or with the 'copper-zinc couple,' which, however, have no action on potassic perchlorate. Potassic chlorate is principally consumed in the manufacture of lucifer matches, and as an oxidizing agent in certain operations of the calico-printer. When added to a solution acidulated with hydrochloric acid, it is often used in the laboratory as an oxidizing agent.

The friction tubes employed for firing cannon are charged with a mixture of

2 parts of potassic chlorate, 2 of antimonious sulphide, and 1 part of powdered glass. A mixture known under the name of *white gunpowder*, consisting of 2 parts of potassic chlorate, 1 part of dried potassic ferrocyanide, and 1 of sugar, has sometimes been manufactured for blasting purposes; but its preparation is attended with very great danger, several fatal accidents having ensued from the facility with which it explodes by friction.

(608) **POTASSIC PERCHLORATE**, or *Perchlorate of potassium*; $KClO_4 = 138{\cdot}6$; *Comp. in* 100 *parts*, K_2O, 33·98; Cl_2O_7, 66·02.—This salt crystallizes in anhydrous prismatic needles, which are very sparingly soluble in cold water; its principal properties and the mode of preparing it have been already described (362). When heated to redness it gives off 46·18 per cent. of oxygen, leaving 53·82 of potassic chloride.

(609) **POTASSIC CARBONATE**, or *Carbonate of potassium*; $K_2CO_3 = 138{\cdot}2$; *Density*, 2·267; *Comp. in* 100 *parts*, K_2O, 68·17; CO_2, 31·83.—This important salt is obtained in large quantities for commercial purposes by lixiviating wood ashes, and evaporating the solution until it crystallizes; the mother-liquor, when it cools, is poured off from the crystallized salts, as it retains the more soluble potassic carbonate, and when evaporated to dryness, affords the *potashes* of commerce, and these, when calcined, yield the impure carbonate known as *pearlash*. Different plants, and different parts of the same plant, when burned, furnish varying quantities of the alkali, which they have extracted from the soil: the leaves and young shoots, where the vital action is the most vigorous, are the parts which furnish the greatest quantity of alkali. Herbaceous plants, therefore, generally furnish more than shrubs, and shrubs more than timber. It appears from the experiments of Violette that the variation of the quantity of crude ash obtained from different parts of the same tree is extremely great. Taking, for instance, the quantity of ash found in the heart-wood as the unit of comparison, the proportion in other parts was as follows:

Heart-wood ...	1	Bark of branches ...	11
Root bark ...	5	Root fibres ...	15
Bark of trunk ...	9	Leaves	25

and it is stated by Chevandier (*Ann. Chim. Phys.*, 1844, [3], x. 129) that the quantity of ash varied as follows for 100 parts of different portions of the wood of the undermentioned trees after drying at 140° (284° F.):

	Solid stem.	Arms.	Small branches.
Beech	0·91	2·15	1·29
Oak	2·43	2·03	1·68
Birch	0·71	1·03	0·60

As an average it may be stated that 1000 parts of timber yield from 2 to 4 parts of pearlash.

In the wine-producing countries, a considerable quantity of

pearlash of good quality is furnished by burning the refuse yeast after the fermentation is complete. The yeast, for this purpose, is pressed, dried in the sun, and burned in shallow inclosures; this dry yeast furnishes nearly 10 per cent. of its weight of the carbonate. Potassium does not exist in plants in the form of carbonate, but occurs in them as salts of different organic acids: these organic acids are destroyed by the action of the heat during incineration, potassic carbonate being produced, whilst the hydrogen and the excess of carbon pass off as water and carbonic anhydride. Various other saline substances are likewise present in the ashes of plants, but those which are soluble consist, in addition to the carbonate, principally of potassic sulphate and chloride: these alkaline salts usually amount to from 10 to 20 per cent. of the entire quantity of ash.

Potassic carbonate is now largely manufactured by the reduction of the sulphate by Leblanc's process in the same way that sodic carbonate is prepared (627), the sulphate being obtained from the potassic chloride by double decomposition with magnesic sulphate:

$$3KCl + 2MgSO_4 = MgSO_4.K_2SO_4 + MgCl_2.KCl.$$

The double magnesic potassic sulphate, $MgSO_4.K_2SO_4$, thus obtained is decomposed by the further action of potassic chloride:

$$MgSO_4.K_2SO_4 + 3KCl = 2K_2SO_4 + MgCl_2.KCl.$$

The artificial *carnallite*, $MgCl_2.KCl$, which is obtained from the mother-liquors, is treated in the same way as the natural carnallite of the Stassfurt mines, so as to recover the potassic chloride it contains. The potassic chloride may also be decomposed by sulphuric acid, but this is not always advantageous, owing to the loss of chloride.

As already noticed, potassic carbonate is manufactured from the residues of the beet-sugar manufacture, and from the potassic salts in wool (p. 411).

A purer carbonate is obtained for chemical purposes by deflagrating a mixture of purified cream of tartar with an equal quantity of pure nitre. The mass is thrown, in small portions at a time, into a red-hot crucible: in this operation the nitre yields oxygen to the vegetable acid, converting its carbon into carbonic acid, which enters into combination with the alkali both of the tartar and of the nitre, whilst the nitrogen is evolved: the carbonate is extracted from the dry mass by lixiviation.

It may also be prepared by mixing 1 part of pure potassic nitrate with 2 of oxalic acid and a little water, and evaporating

to dryness, adding a little more water, and again evaporating and igniting: the carbonate thus prepared contains a little nitrate.

Potassic carbonate is a deliquescent salt, which is with difficulty obtained in oblique rhombic octohedral crystals, $K_2CO_3.2OH_2$. Its reaction with test-paper is strongly alkaline; it has an acrid, alkaline taste. Its solutions have a peculiar odour: 100 parts of water at 15° (59° F.) dissolve 90 of the carbonate; and at the boiling-point take up 205 parts, or rather more than twice their weight, of the salt. Alcohol does not dissolve it. Potassic carbonate fuses by exposure to a red heat, and is partially volatilized at a very high temperature; it is decomposed by silica at a red heat, carbonic anhydride being expelled with effervescence, whilst the silica uniting with the alkali, forms a true silicate, the basis of one of the varieties of glass. Advantage is taken of this property, in the analysis of mineral substances which contain a large quantity of silica, and which are not easily decomposed by the action of acids. For this purpose the mineral to be analysed is reduced to an extremely fine powder by careful levigation; a portion of this powder is accurately weighed, and then intimately mixed with about 3 times its weight of potassic carbonate (or, still better, with thrice its weight of a mixture of $5\frac{1}{2}$ parts of dried sodic carbonate and 7 of potassic carbonate, as this fuses at a lower temperature than either of the carbonates alone); the whole is introduced into a platinum crucible, and exposed to a bright red heat for an hour. The mass enters into fusion, carbonic anhydride escapes with effervescence, and an alkaline silicate is formed, whilst all the bases of the mineral which were combined with the silica are set at liberty. Upon now treating the mass with dilute hydrochloric acid, the silicate is decomposed, the earths and metallic oxides are dissolved, and the silica is partially dissolved and partially separated in the hydrated form. In order to decompose the hydrate of silica, the solution is evaporated to dryness, moistened with hydrochloric acid, and again treated with water; the whole is now placed upon a filter, and the silica, after being well washed, remains behind in a state of purity. The analysis of the filtered liquid is then proceeded with according to the ordinary method adopted for substances directly soluble in acids.

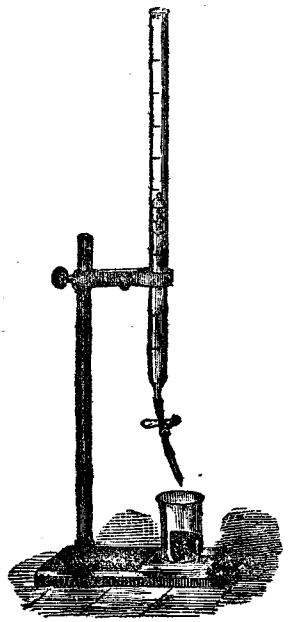
Potassic carbonate is largely consumed in the arts, as for example, in the manufacture of soap and of glass, and for preparing caustic potash and other compounds of potash. It also furnishes the chemist with one of his most indispensable reagents.

(610) **ALKALIMETRY.**—Since the quantity of alkaline

carbonate, technically known as *alkali*, is liable to great variations in different samples of the ash,—and since the commercial value of pearlash depends upon the amount of potassic carbonate which it contains, a rapid and sufficiently accurate method of analysis of this salt becomes a desideratum. For this purpose the process termed alkalimetry is employed; in principle it depends upon the determination of the number of divisions of a dilute acid, of definite strength, which 100 grains of the different samples of ash are capable of neutralizing; the point of neutralization being ascertained by the action of the solution upon blue litmus.

The acid solution which is to be employed is measured from a burette or *alkalimeter*, Mohr's form of which is shown in fig. 338. It consists of a glass tube, with an internal diameter of about five-eighths of an inch, and is sufficiently tall to contain rather more than 1000 grains of distilled water. A little water, say 15 or 20 grains, is introduced into the tube, and the level of its surface marked with a line, numbered 100. 1000 grains of water at 60° F. are then added, and the level of its surface again marked off and indicated as 0; the interval is then subdivided into 100 equal parts, each of which will consequently contain 10 grains of water; opposite every tenth division the number corresponding to it is placed, the numbers increasing from above downwards.

Fig. 338.



The acid is allowed to flow from the burette into a beaker containing the aqueous solution of a known weight of the alkali, until it is quite neutral; the quantity of acid may be regulated with the greatest precision by a glass stopcock, or by means of the spring clamp *s*, shown in fig. 339. The spring is arranged so as to pinch the sides of the caoutchouc tube together, and prevent the escape of liquid; but on compressing the studs between the finger and thumb, the pressure of the spring on the caoutchouc is relaxed to an extent which may be varied at pleasure; and it can be instantly restored by removing the hand and allowing the spring to exert its natural effect.

Erdmann's float, shown in fig. 340, enables the observer

readily to subdivide each division of the burette into tenths; for by reading the level of the liquid at the line, *a*, traced round the float, instead of at the upper curved edge of the liquid, the observation is rendered much more exact.

Various plans have been proposed for preparing the dilute acid; the following will answer the purpose.

The acid preferred is sulphuric. If the pure acid, dihydric sulphate, H_2SO_4, were used, the proportion required would be represented by the proportion of the molecular weights of the two substances:

1 mol. K_2CO_3		1 mol. H_2SO_4		K_2CO_3 grains.		
138·2	:	98	: :	100	:	x (=70·91).

100 grains would therefore contain 70·91 grains of the acid, and a gallon of the diluted acid (70,000 grs.) would contain 70 times

FIG. 339.

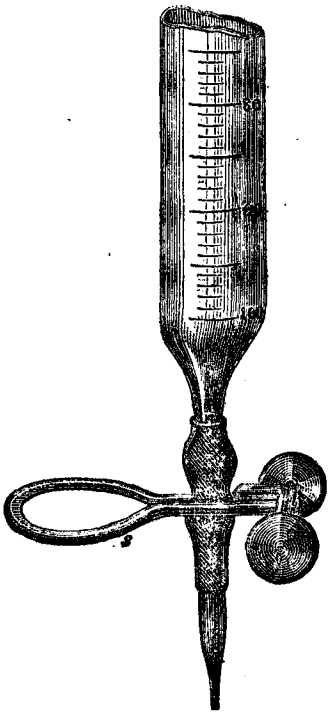


FIG. 340.

this quantity, or 4963·7 grs. The commercial acid, however, is never quite pure, and always contains water, so that about 5000 grains will be requisite. Having weighed out this amount of oil of vitriol, it is to be added cautiously to a quantity of distilled

water, and the volume of liquid, when cool, is to be made up exactly to one gallon. In order to ascertain whether the strength of this alkalimetric acid be accurately adjusted, a quantity of crystallized bicarbonate of potassium is fused in a platinum crucible in order to convert it into the normal carbonate; the fused mass is then poured upon a clean iron plate, and 100 grains of it are quickly weighed, and dissolved in about 3 ounces of water in a small evaporating basin, and tincture of litmus is added in quantity sufficient to colour the solution distinctly blue. Some of the dilute acid is now to be introduced into the alkalimeter until it stands at the mark 0, and is then allowed to run into the solution of potassic carbonate, which is to be gently warmed in order to expel the carbonic anhydride as it is liberated; the acid is cautiously added until the litmus is distinctly but permanently reddened. The acid liquid, if properly diluted, ought to contain, in each division, sufficient sulphuric acid to neutralize 1 grain of potassic carbonate, and the entire 100 divisions of the alkalimeter should therefore exactly produce this effect. If more than 100 divisions of the acid be required, the test acid is too weak; if less than 100 divisions, it is too strong.

Suppose that 95 divisions of the acid were sufficient, the alkalimetric acid from which it was prepared must have contained one-twentieth too much acid; every 95 measures of this acid, therefore, must be diluted with 5 measures of water. If, on the other hand, more acid than 100 divisions be required, say 105 be needed, the acid contains one-twentieth too much water; the quantity of alkalimetric acid used in the experiment requires the addition of one-twentieth more of acid than it originally contained. The alkalimetric acid, when duly adjusted, is preserved in bottles which are accurately closed.

Having thus prepared a test acid of the proper strength, 100 grains of the sample of pearlash for trial are dissolved in 3 or 4 ounces of water, filtered if necessary, and then tested in the same manner: the number of divisions of acid consumed will indicate the per-centage of potassic carbonate present in the sample.

A similar method may be employed to determine the quantity of soda present in any sample of soda ash; but as a certain weight of soda neutralizes a proportionately larger amount of acid than an equal weight of potash, a stronger acid must be used in the alkalimeter.

The quantity of acid required to neutralize 100 grains of pure soda, Na_2O, may be calculated in the following manner:

Na_2O 1 mol.		H_2SO_4 1 mol.		Na_2O grains.		
62	:	98	: :	100	:	x (=158·06).

1000 grains of the dilute acid must therefore contain 158·06 grains of oil of vitriol, and a gallon seventy times this amount, or 11064·2 grains. In practice, 11200 grains may be taken; and the acid tested by means of pure sodic carbonate, obtained by fusing pure sodic bicarbonate. The quantity of sodic carbonate required will be such an amount as contains 100 grains of Na_2O; and this may be ascertained as follows:

Na_2O 1 mol.		Na_2CO_3 1 mol.		Na_2O grains.		Na_2CO_3 grains.
62	:	106	: :	100	:	x (=170·97)

or 1000 grains of the diluted acid should exactly saturate 170·97 grains of pure sodic carbonate. Each division of the alkalimetric acid will then correspond to 1 grain of soda, or 1 per cent. of pure soda in 100 grains of any sample of soda ash. If necessary, the test acid must be corrected by adding more acid or more water until the required strength is exactly attained, in the manner previously described.

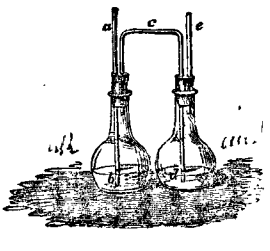
In cases where greater accuracy is required, the acid solution, instead of being measured from the burette, is weighed; and for this purpose, the solution is placed in a light flask of the form shown in fig. 341.

FIG. 341.

In estimating the value of soda ash, which often contains sodic sulphide and thiosulphate, an error might be occasioned by adopting this method; because both the sulphide and the thiosulphate would be decomposed by the sulphuric acid, and as they neutralize it, would be reckoned as sodic carbonate.

The presence of caustic alkali in any sample is easily ascertained by the action of the solution upon argentic nitrate: the carbonates of the alkali-metals occasion a white precipitate of argentic carbonate; but if they contain any caustic alkali, a brown precipitate of hydrated argentic oxide is produced. The presence of sulphides in the ash is immediately manifested by the odour of sulphuretted hydrogen which is evolved on neutralizing the solution with an acid: if any sulphide be present, it will blacken the salts of silver, and interfere with their application as a test for caustic potash or soda.

FIG. 342.



(611) **Process of Will and Fresenius.**—The proportion of carbonic anhydride in any sample of alkali is readily ascertained by means of the apparatus employed for the purpose by Will and Fresenius, represented in fig. 342: *b* is a light flask of about 100 cub. centim. capacity, in which 5 grams of the alkali are placed with about 30 c. c. of water; *d* is a similar flask, in which about 40 c. c. of sulphuric acid is placed. A

sound cork is fitted into the neck of each flask, and is pierced with two apertures for the reception of the tubes, *a*, *c*, and *e*, all of which are open at both ends; the tube, *a*, is sufficiently long to dip into the liquid in the flask; *c* is a bent tube, the longer limb of which passes into the acid in the flask, *d*. The outer extremity of *a* is closed during the experiment by a plug of wax or caoutchouc. The apparatus is charged in the manner already described, and is accurately weighed after it has been connected together. A partial vacuum is now made by applying the mouth to the tube, *e*, and exhausting a portion of the air; on ceasing to exhaust, the acid rises in the tube, *c*, and passes over into *b*, to supply the place of the air which has been withdrawn; effervescence is occasioned by the escape of the carbonic anhydride, which passes off through the tube *c*, and is dried as it bubbles up through the sulphuric acid in the flask *d*. As soon as the effervescence has ceased, a fresh portion of acid is forced over from *d* into *b* by again partially exhausting the air: and this process is repeated until no further effervescence is occasioned by the fresh acid. The plug of wax is now withdrawn from the tube *a*, and a current of air is drawn through the apparatus by exhausting with the mouth at *e*, and the carbonic anhydride is thus completely displaced. The plug is now replaced in the tube *a*, and the apparatus is weighed a second time. The difference between this weight and that obtained on the first occasion, indicates the amount of carbonic anhydride which has been expelled.

If any sulphide or sulphite of the alkali-metal be present, the error which it might occasion by loss of sulphuretted hydrogen, or of sulphurous anhydride, in the gaseous state, and which would be reckoned as carbonic anhydride, is prevented by mixing an equal weight of potassic chromate with the sample under trial: the chromic acid which is liberated by the subsequent action of the sulphuric acid upon the chromate, imparts oxygen to the sulphuretted hydrogen or sulphurous acid, and converts both into sulphuric acid, which would be retained, and would in no way interfere with the result.

(612) **HYDRIC POTASSIC CARBONATE**, *Acid carbonate*, or *Bicarbonate of potassium*; $KHCO_3 = 100{\cdot}1$; *Density*, 2·052.—By passing a current of carbonic anhydride through a strong solution of potassic carbonate, it is slowly converted into the bicarbonate, which is deposited in the form of right rhombic prisms; the action is much more rapid, however, if the gas be passed in under pressure: the crystals are permanent in the air, and require 4 parts of water at 5° (41° F.) for solution. When required perfectly pure and free from chlorides and nitrates, it should be prepared by passing a current of carbonic anhydride through a clear solution of potassic hydrate in alcohol of 80 per cent. until the precipitate becomes pasty; the alcohol is then decanted and replaced by a fresh quantity, the passage of the gas being continued until the precipitate becomes pulverulent. It is then collected, washed thoroughly with alcohol, and dried.

The solution of the bicarbonate, if exposed to the atmosphere, gradually loses one-fourth of its carbonic acid, forming the so-called sesquicarbonate; and if boiled, the same change occurs much more quickly. The acid carbonate is converted into the

normal carbonate when strongly heated. Hydric potassic carbonate has no alkaline reaction upon turmeric. It may be employed for preparing the compounds of potassium in great purity, since, if well crystallized, it is almost absolutely pure, and may be obtained in this state with less difficulty than any other salt of potassium. It is consumed medicinally in considerable quantities, for making effervescing draughts by the addition of citric or tartaric acid to its solution in water.

The *Potassic Silicates* are important compounds in connexion with the manufacture of glass: they will be noticed in treating this subject (632 *et seq.*).

(613) **Characters of the Salts of Potassium.**—The salts of potassium with a colourless acid, are all colourless. They seldom contain any water of crystallization, yet many of them are deliquescent; the carbonate and acetate offer striking instances of this latter peculiarity, and furnish a marked contrast to the corresponding salts of sodium. If pure, the salts of potassium, when introduced upon a platinum wire into the *reducing flame of the blowpipe*, communicate to the outer flame a violet tint; the presence, however, of a small quantity of a salt of sodium masks this effect, in consequence of the strong yellow flame produced under similar circumstances by the compounds of sodium; by means of the spectroscope, however, the potassium is distinctly recognizable, although the sodium salt may be in very large excess. The light emitted by a salt of potassium, in the flame of a Bunsen burner, consists of a feeble continuous spectrum, terminated at one end by a bright line in the red, and at the other by a feebler bright line in the violet (K, fig. 83, Part I. p. 196). Solutions of the salts of potassium yield no precipitate with solutions of the carbonates of the alkali-metals, with potassic ferrocyanide, or with hydric ammonic sulphide. The presence of potassium in solution is recognized by the following characters, provided that no other metal is present except sodium: if the solutions be moderately concentrated, on adding an excess of *tartaric acid* and stirring briskly, a white crystalline precipitate of hydric potassic tartrate, $KHC_4H_4O_6$, is produced, which is readily dissolved upon adding an alkali. *Sodic perchlorate*, and *sodic picrate* have also sometimes been employed as tests for potassium, since both perchloric acid and picric acid (trinitrophenol) form potassium compounds of sparing solubility. These, however, are all soluble to a considerable extent in cold water, and unless tolerably strong solutions are employed, precipitates are not immediately formed. With *silicofluoric acid*, potassium salts yield a transparent gela-

tinous silicofluoride, which forms a white powder on drying. The most conclusive reaction, however, is produced with *platinic chloride;* upon mixing a strong solution of this salt with a concentrated one of a salt of potassium, a yellow double salt, consisting of $2KCl.PtCl_4$, is separated in crystals; it is quite insoluble in alcohol and ether, but is slightly soluble in cold water; it is therefore best for analytical purposes to acidulate the solution suspected to contain potassium with a little hydrochloric acid, and having added a slight excess of the solution of platinic chloride, to evaporate to dryness over the water bath and wash the residue with alcohol as long as anything is dissolved. This salt when heated to redness is decomposed, the platinum loses its chlorine, and the potassic chloride may be dissolved out of the grey residue with cold water, leaving metallic platinum: 100 parts of the chloride of platinum and potassium are equivalent to 16·015 of potassium, or to 19·291 of potassic oxide, K_2O.

§ II. SODIUM: Na=23.

(614) **SODIUM** (Natrium); *Density*, 0·972; *Fusing-pt.* 97°·6 (207°·7 F.).—Sodium may be obtained from its carbonate by a process analogous to that used in procuring potassium, but as the metal does not form a compound with carbonic oxide, it is much more easily prepared. Deville recommends the employment of the following mixture in the extraction of sodium: dried sodic carbonate, 717 parts; powdered charcoal, 175 parts; finely powdered chalk, 108. These materials are mixed intimately and kneaded into a stiff paste with oil, and calcined in a covered iron pot; the mass is then introduced into an iron retort and distilled with the precautions described when speaking of potassium, employing a receiver of the same shape; the dried soda yields about one-ninth of its weight of sodium: the object of adding the chalk is to prevent the charcoal from separating from the sodic carbonate when this salt fuses. The metal is now prepared in considerable quantities by this method, wrought-iron cylinders with moveable ends being substituted for the mercury bottles used in preparing potassium. The iron cylinders are protected from the fire by an exterior cylinder of clay.

As a reducing agent, sodium is but little inferior to potassium in energy, and since its combining number is lower, and the metal is much less expensive, it may generally be advantageously substituted for potassium in such operations.

Sodium has a silver-white colour; in appearance and properties it much resembles potassium, but is somewhat more

volatile; it fuses at a temperature of 97°·6 (207°·7 F.), and burns with a bright yellow flame. Like metallic potassium it must be preserved in some liquid hydrocarbon; Böttger recommends for this purpose a saturated solution of pure naphthalene in petroleum. When dropped into cold water, the metal decomposes a portion of it with evolution of hydrogen, but the gas does not take fire unless the water be previously heated.

The great storehouse of sodium is common salt, which is met with in nature in extensive deposits; it is also contained in vast quantities in the water of the ocean; the immense quantities of soda consumed in the arts are almost exclusively obtained from chloride of sodium, although sodium occurs in several other minerals, such as albite or sodium-felspar, and cryolite, the double fluoride of sodium and aluminium. Borax or the acid borate of sodium, and trona or the sesquicarbonate, as well as the nitrate, are also native compounds of sodium.

(615) **SODIC HYDRIDE**, $NaH_2 = 25$.—This compound, prepared in the same way as potassic hydride (589), is as soft as sodium at the ordinary temperature, but becomes brittle a little below its melting-point. It is of silvery aspect, and less alterable by exposure to air than the potassium compound. Its density is 0·959. Unlike potassic hydride, the sodium compound dissolves only small quantities of hydrogen.

(616) **SODIC CHLORIDE**, or *Chloride of sodium;* NaCl = 58·5; *Density*, 2·24; *Comp.* in 100 *parts*, Na, 39·32; Cl, 60·68.—This important and well-known compound, formerly called *muriate of soda*, constitutes common culinary table-salt. It is found native in the solid form, and it exists in solution in sea water in a proportion of about 2·7 per cent., which amounts to rather more than four ounces per gallon, or to a bushel in from 300 to 350 gallons.

The extraction of the chloride from sea water was formerly practised to some extent upon the southern coast of our own island: in Great Britain this mode of manufacture is now unimportant, although in the southern countries of Europe the preparation of bay-salt is still a branch of industry of some magnitude. In conducting this process the sea water is allowed to run into shallow pools, in which the water evaporates and the liquor becomes concentrated by the heat of the sun; crusts of the salt are formed, and are raked off from time to time: the rough crystals thus obtained being the *bay-salt* of commerce. The concentrated sea water, or *bittern*, is employed as a source of bromine.

Balard, who has devoted much attention to the study of these mother-liquors, has devised a method of extracting from them not only sodic sulphate, but also

an important quantity of salts of potassium, in the form of a magnesic potassic sulphate, $MgK_2SO_4.6OH_2$, as well as of a magnesic potassic chloride, $KCl.MgCl_2.6OH_2$. The process requires a careful attention to the temperature at which the crystallizations are effected. At temperatures below $-3°$ (26°·6 F.), the chloride of sodium still present in the brine decomposes the magnesic sulphate, with formation of magnesic chloride, and sodic sulphate; whilst at temperatures above 38° (100°·4 F.), a sparingly soluble sodic magnesic sulphate, $Na_2Mg2SO_4.6OH_2$, is formed. The following is the modification of Balard's plan, now adopted by M. Merle at Carmargue (*Les Mondes*, January, 1866, p. 76). Sea water is concentrated in the salt-pans by spontaneous evaporation. Three different saline deposits are thus obtained; the first of these consists entirely of sodic chloride, and continues to be formed until the liquor acquires a density of 1·267. The second deposit, known as *mixed salt*, then makes its appearance, and continues to separate until the liquor attains a density of 1·3. It consists of common salt and magnesic sulphate in equal quantities. The third deposit, which is formed between the densities of 1·3 and 1·32, is the *summer salt*. It contains the whole of the potassium, partly in the form of magnesic potassic sulphate, partly as magnesic potassic chloride, mixed with sodic chloride and magnesic sulphate. The *mixed salt* is redissolved, and the concentrated solution cooled down artificially by the use of Carré's refrigerator (*note*, Part I., p. 387) until the temperature falls to $-4°$ (24°·8 F.). As the liquor passes through the refrigerator, crystallized sodic sulphate is deposited in nearly a pure state, and is dried in a centrifugal hydro-extractor. The mother-liquor retains magnesic chloride, and is preserved. The crude *summer salt* is redissolved in a small quantity of water heated to 90° or 100° (194° or 212° F.), and on cooling it deposits rather more than half the potash as potassic magnesic sulphate, $K_2Mg2SO_4.6OH_2$. The mother-liquor retaining chlorides of sodium and potassium with magnesic sulphate is cooled down to $-15°$ or $-18°$ (5° or 0°·4 F.), by which more sodic sulphate is separated. The saline liquor is finally boiled down to a density of 1·331, and deposits nearly all the remaining sodic chloride. The hot liquor is run into shallow coolers, where it deposits the whole of the potash in the form of the magnesic potassic chloride, $KCl.MgCl_2.6OH_2$. On treating this with half its weight of water, the salt is decomposed, the deliquescent magnesic chloride is dissolved, together with one-fourth of the potassic chloride, and the solution is returned to be recrystallized with the fresh mother-liquor, whilst the undissolved potassic chloride is ready for sale after it has been dried.

The latest improvement in the treatment of bittern consists in mixing the hot mother-liquors with a boiling solution of magnesic chloride: this causes the precipitation of a mixture of magnesic sulphate and common salt, which is treated like the *mixed salt*, whilst the mother-liquors from these, on cooling, deposit a double chloride of magnesium and potassium.

Immense beds of common salt are met with in Cheshire, at Wielitzka in Poland, in the Salzkammergut in Austria, and at Cardona in Spain. It has also recently been found in abundance in the north of Ireland, near Belfast, and on the southern borders of the Durham coal-field. Near Northwich, the principal deposit of rock-salt in England, the mineral occurs in two beds, situated one above another, separated by about 9 metres, or 30 feet, of clay and marl intersected with small veins of salt: the two beds together are not less than 18 metres or about 60 feet in thickness, 274 metres or 300 yards broad, and a mile and

a half long. These beds occur in magnesian limestone. The celebrated and beautiful mine of Wielitzka contains sufficient salt to supply the entire world for ages. It is calculated that the mass of rock-salt here is 500 miles in length, 20 miles broad, and not less than 1200 feet (366 metres) in thickness. This salt deposit occurs in the chalk formation.* There is also said to be a large bed of it in Scinde, 20 miles long and 15 miles broad. Sodic chloride is sometimes found crystallized, and is then termed *sal gem*, or *rock-salt*. Where fuel is cheap, the solubility of the chloride is frequently taken advantage of in diminishing the labour of raising the salt to the surface, water being let down into the bed of salt and allowed to remain until it has become saturated: it is then pumped out and the brine is boiled down and crystallized.

Some brine springs contain too small a portion of salt to render it profitable to effect the evaporation by heat; the water in these cases is concentrated by *graduation*, in the manner practised at Reichenhall, near Salzburg; this process consists in exposing a large surface of the brine to the air, by pumping it up to a height, and then allowing it to trickle slowly over large stacks of fagots, piled in suitable buildings screened from rain, but freely exposed to the prevailing wind: after this process has been repeated eight or ten times, the solution acquires a density of about 1·140, and is then sufficiently concentrated to allow the evaporation to be finished as usual by the direct application of heat. In the first basin an insoluble precipitate, chiefly consisting of the sodic calcic sulphate, is deposited, Na_2Ca2SO_4, partly in the form of mud, or *schlot* as the Germans term it, partly in the form of a hard scale, which adheres to the bottom of the pan: when the liquor reaches a density of 1·236, it is decanted into another pan and evaporated; the crusts of salt are removed as they are formed.

The appearance of the salt varies according to the rate at which the evaporation is conducted; when the brine is boiled down rapidly, it furnishes the mealy, fine-grained salt used upon our tables; if evaporated more slowly, the hard, crystallized salt preferred for fishery purposes is obtained. The salt of commerce always contains a certain proportion of magnesic chloride, which gives it a slightly deliquescent character, and adds to the pungency of its flavour. It is stated, that when the proportion of magnesic chloride in the brine is considerable, the crystals of sodic chloride form a scum over the surface which much retards the evaporation. This inconvenience may be remedied by the addition of a quantity of sodic sulphate, which decomposes the magnesic chloride and converts it into sulphate.

Properties.—Sodic chloride has an agreeable saline taste. It crystallizes in colourless transparent cubes, which are anhydrous.

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* Some specimens of the salt from this mine decrepitate when thrown into water, owing to the escape of condensed gas ($P CH_3$; Rose), which is liberated during the solution of the crystals.

When heated suddenly, the crystals decrepitate with violence; at a bright red heat they fuse, and by a stronger heat are converted into vapour. It is soluble in about 3 parts of cold water, and scarcely more soluble at a temperature of 100° (212° F.); the saturated solution has a density of 1·205. Water at 0° (32° F.) dissolves 35·5 per cent. of the salt, and 41·2 per cent. at 109°·5 (229°·1 F.), the boiling-point of the solution. Although readily soluble in water, it is much less soluble in hydrochloric acid, resembling in this respect many other chlorides; so that on adding hydrochloric acid to a saturated solution of the salt, a large portion is thrown down in the crystalline state. Sodic chloride is insoluble in pure alcohol, but is taken up in considerable quantity by dilute spirit. By exposing a dilute aqueous solution of the salt to a low temperature, ice is deposited at temperatures varying with the strength of the solution; a solution containing 26·27 per cent. of salt behaves differently, for on cooling it to −7° (19°·4 F.) a hydrate, $NaCl.2OH_2$, separates in hexagonal tables; as the temperature rises, these crystals fall to pieces, and become converted into a heap of minute cubes, water being separated (comp. Pt. I. p. 126).

Sodic chloride is consumed in large quantities in the manufacture of the salts of sodium; it is extensively employed in glazing stoneware, and is an article of daily domestic use, being indeed an essential constituent of the food both of man and of animals, who languish if it be supplied in insufficient quantity. The process of salting meat is resorted to on account of the powerfully antiseptic qualities of sodic chloride. In this operation a large quantity of the nutritive juice of the meat is extracted, and this liquid when saturated with the salt forms the *brine*. Meat thus prepared is much less digestible and nutritious than fresh meat.

Sodic chloride, when fused with rather more than one-third of its weight of sodium in a current of dry hydrogen, furnishes a blue compound, supposed to be a subchloride, Na_2Cl (Bunsen).

(617) **SODIC BROMIDE,** or *Bromide of sodium:* NaBr = 103; *Density,* 3·08—This salt is analogous to potassic bromide; it is soluble both in water and in alcohol, and crystallizes at temperatures above 30° (86° F.) in anhydrous cubes: at lower temperatures it forms hexagonal tables with $2OH_2$.

(618) **SODIC IODIDE,** or *Iodide of sodium:* NaI = 150; *Density,* 3·45; this crystallizes at temperatures above 40° (104° F.) in cubes, which are anhydrous; but if crystallized at ordinary temperatures it yields large transparent, striated, oblique rhombic prisms, with $2OH_2$. Sodic iodide occurs native in sea-water in minute proportion, but small as this proportion is, it furnishes the commercial supply of iodine: many marine plants assimilate it, and when these plants are burned, the iodide remains in the residue: the ash thus obtained goes by

the name of *kelp*. A ton of good Irish kelp from drift-weed furnishes about 8 lb. of iodine.

(619) **OXIDES OF SODIUM.**—The metal forms two well-known oxides, one of which contains twice as much oxygen as the other:

				Sodium.		Oxygen.		
Soda	Na_2O	= 62		74·19	+	25·81	=	100
Sodic peroxide ...	Na_2O_2	= 78		58·97	+	41·03	=	100

A blue suboxide is said also to exist.

Sodic Oxide, or *Soda*, $Na_2O=62$, forms the base of the important series of salts of sodium. It can be procured in the anhydrous state by burning the metal in dry air or in oxygen gas: it is of a yellowish-white colour, attracts moisture as greedily as the corresponding oxide of potassium, forming sodic hydrate, NaHO, from which the water cannot be again expelled by heat.

Sodic Dioxide, Na_2O_2, obtained by igniting sodium in oxygen is of a pure white colour, and dissolves in water with development of great heat, but with only a very slight evolution of gas.

(620) **SODIC HYDRATE**, or *Caustic Soda*, NaHO=40; *Comp. in* 100 parts, Na_2O, 77·5; OH_2, 22·5.—In appearance and properties *sodic hydrate* closely resembles the corresponding potassium compound; it may be formed from the carbonate or nitrate by methods similar to those employed for preparing potassic hydrate; its action upon acids, however, is less energetic. According to Filhol the solid hydrate, NaHO, has a density of 2·13. The following table shows the proportion of anhydrous soda which is contained in solutions of sodic hydrate of different densities:

Strength of Solutions of Caustic Soda at 15° (59° F.) (*Tünnermann*).

Density.	Na_2O in 100 parts.	Density.	Na_2O in 100 parts.	Density.	Na_2O in 100 parts.
1·4285	30·220	1·2982	20·550	1·1528	10·275
1·4193	29·616	1·2912	19·945	1·1428	9·670
1·4101	29·011	1·2843	19·341	1·1330	9·066
1·4011	28·407	1·2775	18·730	1·1233	8·462
1·3923	27·802	1·2708	18·132	1·1137	7·857
1·3836	27·200	1·2642	17·528	1·1042	7·253
1·3751	26·594	1·2578	16·923	1·0948	6·648
1·3668	25·989	1·2515	16·319	1·0855	6·044
1·3586	25·385	1·2453	15·714	1·0764	5·440
1·3505	24·780	1·2392	15·110	1·0675	4·835
1·3426	24·176	1·2280	14·506	1·0587	4·231
1·3349	23·572	1·2178	13·901	1·0500	3·626
1·3273	22·967	1·2058	13·297	1·0414	3·022
1·3198	22·363	1·1948	12·692	1·0330	2·418
1·3143	21·894	1·1841	12·088	1·0246	1·813
1·3125	21·758	1·1734	11·484	1·0163	1·209
1·3053	21·154	1·1630	10·879	1·0081	0·604

Caustic soda, which is extensively used in the manufacture of hard soaps, is now manufactured on a large scale in the alkali works, which supply it in the form of a solid hydrate containing 60 per cent. of anhydrous soda; for this purpose advantage is taken, as proposed by Mr. Gossage, of the caustic soda present in the solutions of crude soda.

In order to separate it, the crude solution obtained from the black-ash vats is evaporated down until it acquires a density of 1·5 or 1·6, during which operation almost all the carbonate, sulphate, and chloride of sodium crystallize out. The solution (technically known as *red liquor*) is of a red colour, owing to the presence of a peculiar soluble compound of sulphide of sodium and sulphide of iron, and is likewise contaminated with ferrocyanide, and occasionally with sulphocyanide of sodium. By forcing air under pressure for several hours through the hot liquid, the iron is precipitated as sesquioxide, and the sulphur compounds are converted into sulphates. The completion of the oxidation is effected by the addition of sodic nitrate. The entire process of oxidation may indeed be more rapidly effected by means of the nitrate. After its addition the evaporation is carried further, until the mass by degrees becomes heated nearly to redness. When the temperature rises to 155° (311° F.), large quantities of ammonia are evolved, and subsequently, as the heat becomes much greater, nitrogen escapes abundantly (Pauli). The ammonia is produced partly by the decomposition of the cyanogen compounds, but also in part from the removal of oxygen from water by the sulphides, whilst the hydrogen reduces the nitric acid to the form of ammonia. The fused soda is poured into sheet-iron vessels, in which it solidifies, and is preserved for the market. (*Hofmann's Jury Report, Int. Exhib.* 1862, p. 28.)

(621) **SULPHIDES OF SODIUM.**—These correspond in number with those of potassium, which they closely resemble. They may be prepared by analogous methods. The *monosulphide* may be obtained in octohedral crystals of the formula $Na_2S.9OH_2$.

(622) **SODIC SULPHATE,** or *Sulphate of sodium*; $Na_2SO_4.10OH_2 = 142 + 180$; *Density, anhydrous*, 2·597; *cryst.* 1·469; *Comp. in 100 parts* of dry salt, N_2O, 43·67; SO_3, 56·33; of crystallized salt, Na_2O, 19·26; SO_3, 24·84; OH_2, 55·90.—This salt has long been known under the name of *Glauber's salt.* It crystallizes usually in long four-sided prisms, terminated by dihedral summits. It is remarkably efflorescent, and loses the whole of its 10 molecules of water by mere exposure, at common temperatures, to the atmosphere. It has a saline, bitter taste, and is occasionally used medicinally as a purgative.

The solubility of sodic sulphate in water offers some remarkable anomalies (55), which have been the subject of many inquiries, the most complete of which are those of Löwel.* It has

* Three forms of sodic sulphate may be obtained in crystals—viz., 1. the anhydrous sulphate; 2. the ordinary crystallized sulphate with $10OH_2$; and 3. the hydrate with $7OH_2$, which crystallizes in rhombic prisms. Each of these

already been mentioned (74) that a boiling saturated solution of this salt, if closed hermetically, may be kept for months without crystallizing, but the moment that air is admitted, the whole generally becomes semi-solid, from the sudden formation of crystals through the mass. When this does not happen the crystallization may always be instantly determined by dropping in a fragment of the sulphate, or by contact with a rod of glass

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varieties has a specific solubility. The following table (Löwel, *Ann. Chim. Phys.*, 1857, [3], xlix. 50) exhibits the varying solubility of each form of sodic sulphate, as the temperature rises:

100 *Parts of Water when saturated contain, of*

Temperature.		Anhydrous salt.		Salt with $10OH_2$.		Salt with $7OH_2$.		
°C.	°F.	Anhydr.	with Anhydr. $= 10OH_2$.	Anhydr.	with Anhydr. $= 10OH_2$.	Anhydr.	with Anhydr. $= 7OH_2$	with $= 10H_2O$.
0	32			5·02	12·16	19·62	44·84	59·23
11·67	53·0			9·00	23·04	30·49	78·90	112·73
13·30	55·9			13·20	35·96	37·43	105·79	161·57
17·91	64·4	53·25	371·97	16·80	48·41	41·63	124·59	200·00
25·05	77·1	52·76	361·51	19·40	58·35	44·73	140·01	234·40
28·76	83·8	51·53	337·16	28·00	98·48	52·94	188·46	365·28
30·75	87·3	51·31	333·06	30·00	109·81	54·97	202·61	411·45
31·84	89·3	50·37	316·19	40·00	184·09			
32·73	90·9	49·71	305·06	50·76	323·13			
33·88	93·0	49·53	302·07	55·00	412·22			
40·15	104·3	48·78	290·00					
45·04	113·1	47·81	275·34					
50·40	122·7	46·82	261·36					
59·79	139·6	45·42	242·89					
70·61	159·3	44·35	229·87					
84·42	184·0	42·96	213·98					
103·17	217·7	42·65	210·67					

From this table it appears that the solubility of the anhydrous salt decreases from 17°·9 C. to the boiling-point (103°·17 C.) of the solution. Below 17°·9 C. the molecular constitution of the salt is changed, a saturated solution depositing in vessels from which air is excluded, crystals of the 7-atom hydrate, 100 parts of water at 17°·9 C. retain as much as 53·25 of the anhydrous salt, whilst at the boiling-point only 42·65 parts are held in solution. Hence if a solution saturated at 17°·9 C. be simply heated to boiling, without allowing any loss of liquid by evaporation, it will deposit in hard, gritty, anhydrous crystals more than one-fifth of the salt which it previously held in solution.

In the case of the 10-molecule hydrate, the solubility increases until the temperature reaches 33°·9 C., at which point the salt begins to liquefy in its water of crystallization; its molecular constitution then undergoes a change, and it becomes gradually converted into the anhydrous variety, which at that particular temperature has a lower solubility than the hydrated salt, and consequently is partially separated in crystalline grains.

The hydrate with $7OH_2$ is more soluble than either of the foregoing forms; but under ordinary circumstances it cannot exist in contact with the atmosphere,

or of metal. If, however, the glass rod or the metallic wire be boiled with water, and allowed to cool under water or in a closed vessel, kept chemically clean in short (Tomlinson), or if it be strongly heated, it may be introduced into the supersaturated solution without causing the crystallization of the salt. According to Gernez and Coppet (*Compt. Rend.*, 1870, lx. 833; *ibid.*, 1874, lxxviii. 194, 283, and 499), although the anhydrous sulphate, obtained by exposing the crystals of the hydrated salt to the air at the ordinary temperature, produces immediate crystallization when introduced into a supersaturated solution of the sulphate, yet if it has been dried at temperatures above 33° (91°·4 F.) it does not do so, and may even be dissolved in cold water so as to form a supersaturated solution of the ordinary salt. This fact renders it highly probable that in supersaturated solutions of the sulphate, the salt exists in the anhydrous form, and that crystallization occurs when any circumstance occasions the formation of the less soluble 10-molecule hydrate.

Crystallized sodic sulphate is soluble in hydrochloric acid, with great depression of temperature. A convenient freezing

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and is only deposited from supersaturated solutions in closed vessels, or in flasks, which have been allowed to cool covered with small capsules, so as to prevent the entrance of particles of dust or of foreign matter. Crystals of the 7-molecule hydrate may also be obtained by pouring a boiling solution of the sulphate into a capsule and allowing it to cool under a bell-glass, over a vessel of calcic chloride. In whatever mode the crystals of the 7-molecule hydrate have been produced, they undergo change from very slight causes, and become white and opaque with evolution of heat, either when exposed to the air, or when the solution is allowed to crystallize around them, or when touched with a glass rod. The solubility of the 7-molecule hydrate rises with the temperature, as is shown in the table; but this form of the salt cannot exist at temperatures above 29° C.; for when heated to this point its crystals begin to liquefy in their water of crystallization; and, in consequence of a molecular change, crystals of the anhydrous variety are deposited.

From the foregoing details it will be easy to perceive why it is that a hot solution of the sulphate deposits crystals so slowly:—When a solution of sodic sulphate, saturated at its boiling-point, is poured into an open capsule, a film of crystals of the anhydrous sulphate is formed at first upon its surface, owing to the rapid evaporation of a portion of the solvent. No crystals, however, are deposited in the body of the liquid until the temperature has fallen to about 33° C. The film of crystals first formed is gradually redissolved, and crystals of the 10-molecule hydrate are formed as the temperature continues to fall. If the solution be evaporated at temperatures above 34° C., acute rhombic octohedra of the anhydrous salt are produced: but if a boiling saturated solution be allowed to cool in closed vessels, no crystals are deposited until the temperature falls to 17°·9 C., when oblique rhombic prisms of the 7-molecule hydrate are formed.

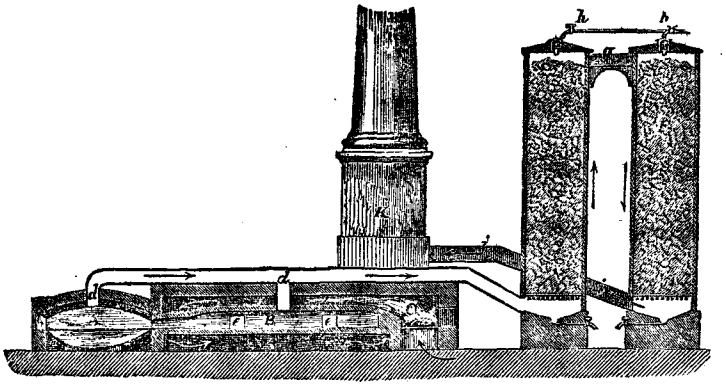
mixture is obtained by pouring 5 parts of the commercial acid upon 8 of the crystallized sulphate.

Native sodic sulphate, to which the name of *Thénardite* has been given, has been met with nearly pure not far from Madrid, deposited at the bottom of some saline lakes, in anhydrous octohedra. It has likewise been found, not far from the same place, combined with calcic sulphate, as *Glauberite*, in anhydrous oblique prisms of the formula Na_2Ca2SO_4.

Crystallized sodic sulphate also frequently occurs in needles as an efflorescence upon plaster, and upon brickwork in damp situations.

Preparation.—Sodic sulphate is made from oil of vitriol and common salt in enormous quantities, under the name of *salt-cake*, as a preliminary step in the manufacture of soda ash. The operation is carried on in a reverberatory furnace, connected with an apparatus for condensing the hydrochloric acid, which, until within the last few years, was allowed to escape into the atmosphere, to the serious injury of vegetation in the surrounding district. One of the best forms of furnace is shown in section in fig. 343: the course of the flues, however, is not exactly such as is there represented: A, the smaller of the two compartments

FIG. 343.



which compose the furnace, is of cast iron; into this (the *decomposer*) from 5 to 6 cwt. (about 250 or 300 kilos.) of common salt are introduced, and rather less than an equal weight of *brown* sulphuric acid, of density 1·78, is gradually mixed with it, a gentle heat being applied to the outside; an enormous quantity of hydrochloric acid gas is disengaged, and passes off by the flue, *d*, to the condensing towers, E and F; these towers are filled with fragments of broken coke or stone, over which a continuous stream of water is caused to trickle slowly from *h*, *h*. A steady current of air is drawn through the furnace and condensing towers, by connecting the first tower with the second, as repre-

sented at *g*, and the second tower with the main chimney, K, of the works. In the first bed of the furnace, about half the hydrochloric acid is expelled from the salt, the reaction being, $2NaCl + H_2SO_4 = NaCl + NaHSO_4 + HCl$: the pasty mass thus produced, which consists of a mixture of acid sulphate of sodium and undecomposed salt, is then pushed through a door for the purpose into the *roaster*, or second division, B, of the furnace.

In the second stage of the operation a higher temperature is required; the acid sulphate of sodium then reacts upon the unchanged chloride, and the conversion into normal sodic sulphate is complete; thus $NaCl + NaHSO_4 = HCl + Na_2SO_4$. The hydrochloric acid gas, as it is liberated from B, passes off through the flue *d*, and is carried on to the condensing towers. Heat is applied to the outside of the roaster, B; the smoke and products of combustion circulate in separate flues around the chamber, in the direction indicated by the arrows, but never come into contact with the salt-cake in B.

(623) **SODIC TRIPOTASSIC DISULPHATE**; $NaK_32SO_4 = 332{\cdot}3$, Penny; *Density*, 2·668.—This double salt is anhydrous; it may be formed by dissolving the two salts in water, and evaporating. Gladstone has shown that the employment of a large excess of sodic sulphate does not alter the composition of the salt, the excess of sodic sulphate crystallizing in its usual form.

It is obtained upon a large scale from kelp liquors during the manufacture of iodine, and is known under the name of *plate sulphate*, from the manner in which it is deposited in hard crystalline layers or plates, upon the sides of the crystallizing vats. During the act of crystallizing it emits vivid scintillations of phosphorescent light: this phosphorescence is most striking when the temperature is near 40° (104° F.). A very brilliant effect is produced by dashing a pailful of the warm mother-liquor upon a crop of crystals in a vat from which the mother-liquor has been drained off a few hours previously.

(624) **HYDRIC SODIC SULPHATE**, *Acid sulphate of sodium*, or *Bisulphate of soda* ($NaHSO_4 = 120$; *Density*, 2·742) corresponding to the hydric potassic sulphate, may be formed. It is more easily deprived of basic hydrogen by heat than the acid sulphate of potassium; $2NaHSO_4$ yielding $Na_2S_2O_7 + OH_2$. The *sodic pyrosulphate* thus formed loses its sulphuric anhydride at a higher temperature, and may hence be employed as a convenient source of this anhydride (428).

A *sodic quadrisulphate*, $Na_2SO_4.3SO_3.6OH_2$, corresponding to the potassium compound has been obtained: the crystals melt at 90° (194° F.).

(625) **SODIC SULPHITE**, or *Sulphite of sodium*, $Na_2SO_3.10OH_2 = 126 + 180$; *Density*, 1·736.—This salt is now prepared largely under the name of *antichlore*, for the purpose of removing the last traces of chlorine from the bleached pulp obtained from rags in the manufacture of paper. It is procured by passing sulphurous anhydride, obtained by the combustion of

sulphur in air, over moistened crystals of sodic carbonate, so long as the gas is absorbed; the mass is dissolved in water and crystallized. Sodic sulphite forms efflorescent, oblique prisms, which fuse at 45° (113° F.); they are soluble in about 4 parts of cold water, forming a solution which has a slightly alkaline reaction and a sulphurous taste.

A *Hydric sodic sulphite,* or *Acid sulphite of sodium,* may be obtained in crystals, either as $NaHSO_3$, or with $4OH_2$.

(626) **SODIC NITRATE,** *Nitrate of sodium,* or *Cubic nitre,* $NaNO_3=85$; *Density,* 2·26.—This occurs abundantly from 0·6 to 1·0 metre below the surface of the soil near Iquique, in the district of Atacama, in Peru, and at Tarapaca in Northern Chili. It is a somewhat deliquescent salt, and is soluble in less than twice its weight of cold water [100 parts of water dissolve 80 of the nitrate at 15° (59° F.)]: it crystallizes in obtuse rhombohedra, and has a cooling, saline taste. When heated, it fuses at 310°·5 (591° F.), and undergoes decomposition at a higher temperature. It is employed in the manufacture of nitric and sulphuric acids, but from its deliquescent nature it cannot be substituted for potassic nitrate in gunpowder. It is frequently used as a manure, as in top-dressing barley. Large quantities of sodic nitrate are converted into saltpetre by treating the sodic nitrate with potassic chloride in equivalent quantity (p. 419).

(627) **SODIC CARBONATE,** or *Carbonate of sodium;* $Na_2CO_3.10OH_2=106+180$; *Density, anhydrous,* 2·466; *cryst.* 1·423; *Comp. in* 100 *parts* of dry salt, Na_2O, 58·49; CO_2, 41·51: cryst. OH_2, 62·93; Na_2O, 21·68; CO_2, 15·39.—The preparation of this salt constitutes one of the most important branches of chemical manufacture in this country, immense quantities of it being consumed in the production of glass, in the fabrication of soap, and in the preparation of the various compounds of sodium, besides a considerable consumption as a detergent by the calico-printer, as well as in the laundry for softening hard waters by precipitating the salts of calcium and magnesium. From their lower price, compounds of sodium are now often employed where potassic salts were formerly, but there are a few cases in which this is not practicable: potassic nitrate, for instance, is still required in the manufacture of gunpowder; in the finest varieties of glass, potash is used, as soda produces a green tint; and potassic chlorate, dichromate, and tartrate, as well as the cyanogen compounds of potassium, are still preferred to the corresponding salts of sodium.

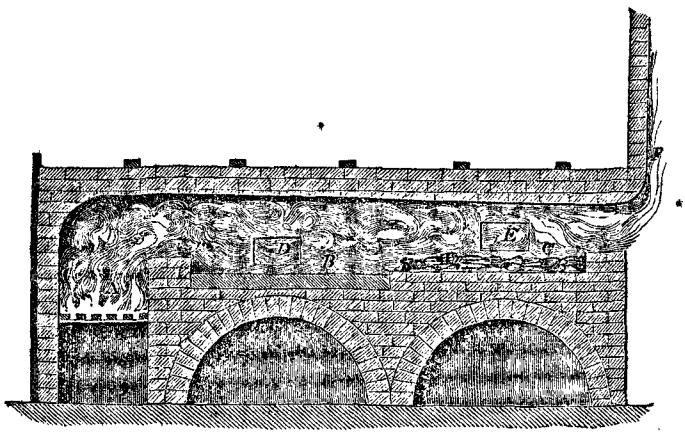
The greater portion of the sodic carbonate formerly employed

was obtained from *barilla*, which is the ash furnished by burning marine plants. The *Salsola soda* was extensively cultivated for this purpose on the southern coast of Spain; on being burnt it yields a semi-vitrified mass, which contains from 25 to 30 per cent. of normal sodic carbonate. The *Salicornia* was cultivated for a similar purpose on the southern coast of France; but these sources have been almost entirely superseded by a process devised by Leblanc, by which the carbonate may be manufactured from sea-salt.

Manufacture of Sodic Carbonate.—In the process of manufacture a rough sodic sulphate is first formed, in the manner already described (622). This sulphate is then mingled with chalk and powdered coal in the proportion of about 3 parts of the sulphate, 3 of chalk, and $1\frac{1}{2}$ or 2 of coal; this mixture is thrown, in quantities of about $2\frac{1}{2}$ cwt., or 125 kilos., at a time, into a hot reverberatory furnace, and frequently stirred, until the mass is thoroughly melted.

The furnace, fig. 344, is constructed with two doors, D, E, and a double floor, B, C; one charge is introduced at the further door, E, whilst another, nearer the fire, is fusing at B: towards the con-

FIG. 344.

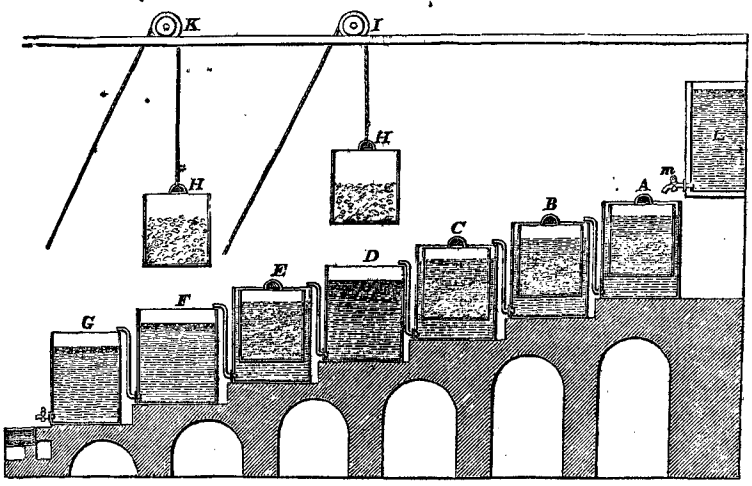


clusion of the operation the mass melts, and effervesces violently from the escape of carbonic oxide gas, which burns with a greenish or yellow flame; the mass is stirred briskly for a few minutes, and when completely and tranquilly fused, is raked out into a square trough or mould; when cold, this loaf is turned out and forms *ball soda*, or *black-ash*, containing from 20 to 27

per cent. of sodic oxide, mixed with calcic sulphide, quicklime,* and unburned coal. In order to extract the salts of sodium from it, the black ash is broken up into coarse fragments, and digested with warm water for six hours, in vats provided with false bottoms: this washing is systematically carried on until the soluble portions are entirely extracted, the last washings being employed to act upon fresh portions of ball soda.

One of the forms of apparatus for the lixiviation of ball soda is shown in fig. 345. The principle on which it is constructed is simple, but it admits of extensive application; for in many cases much of the economy of a manufacturing process depends upon the systematic washing of the product in such a manner as to extract the largest amount of soluble matter by means of the smallest quantity of water, in order to reduce to a minimum the time and quantity of fuel required to effect the subsequent evaporations. In the case before us, this was formerly effected by placing the material for lixiviation—the black ash—in perforated

FIG. 345.



sheet-iron vessels, H, H, which could be raised or lowered into outer lixiviating vessels, also made of iron, by means of the cords and pulleys I, K. When a charge was received from the furnace it was introduced into the lowest vessel, G, where it was submitted to the dissolving action of a liquid already highly charged with alkali by digestion upon the black ash contained in the tanks above it; after a certain time this charge was raised by the rope from G into the tank F, where it was submitted to a weaker liquid, and so on, successively. The alkali at each stage became more completely exhausted, and the residue was successively submitted to the action of weaker ley, until at length, in A, it was acted upon by water only, supplied from the cistern L. When fresh water was admitted from *m*, to

* It is at present quite undecided whether the black ash contains a mixture of calcic oxide and sulphide or a calcic oxysulphide, $CaO.2CaS$; but the former view appears to be the most probable.

the top of the vessel, A, as it is specifically lighter than the saline solution, it remains on its surface, and gradually displaces the solution from A, through the bent tube, whilst the water takes its place; the liquid from A acts in a similar manner upon that contained in B; and this displacement proceeds simultaneously through each successive tier of the arrangement, until the concentrated ley flows off from G, and is transferred to the evaporating pans. A still more convenient arrangement, in which all the tanks are upon the same level, is now in common use in the alkali works of this country. The charge after it has once been introduced into the tank is not removed again until completely exhausted. By a suitable arrangement of pipes each tank can be made in succession the recipient of the fresh water, or of leys of gradually increasing strength derived from the neighbouring tanks; advantage being taken of the fact, that as the solution becomes more highly charged with the soluble material, the height of the column, or the water-level, in each successive vat stands progressively lower, until the liquid flows off saturated; and thus a continuous flow of liquid through the system is maintained. One of the great advantages of this modification of the extracting process is that the black ash is not disturbed and broken up as it is when mechanically transferred from one vessel to another, so that the extraction is not only more complete, but is performed more rapidly. (*Chemical Technology, Richardson & Watts*, 2nd ed. vol. i. part iii. p. 267.)

Almost the whole of the sulphur originally present in the salt-cake is retained in the insoluble residue in the form of calcic sulphide, together with the excess of lime and coal employed. It often accumulated at the soda works until it formed a mountain of *soda waste*, to the annoyance both of the neighbourhood and of the manufacturer; much of the sulphur may be recovered from this waste, however (p. 450), and some of it is utilized for the preparation of sodium thiosulphate (hyposulphite of soda) (433).

The water for lixiviation must not be employed at a temperature exceeding 44° (111°·2 F.), otherwise the calcic sulphide is decomposed into a mixture of calcic sulph-hydrate, which is soluble, and calcic hydrate; $2CaS + 2OH_2$ becoming $CaS.SH_2 + CaO.OH_2$, and this sulph-hydrate immediately reacts upon the sodic carbonate, furnishing disodic sulphide and calcic carbonate, whilst the hydrosulphuric acid converts the sodic hydrate into disodic sulphide: $CaS.SH_2 + Na_2CO_3 + 2NaHO = 2Na_2S + CaCO_3 + 2OH_2$.

The black solution obtained by the lixiviation of the black ash is allowed to settle, and is then pumped up into large shallow iron pans, where it is evaporated by the waste heat from the black-ash furnaces. A large portion of the salt crystallizes during the ebullition, and is removed by means of perforated ladles. In order to convert the caustic soda which the mother-liquor contains into carbonate, it is evaporated to dryness, and after being mixed with about a seventh of its weight of sawdust, is roasted in a reverberatory furnace: most of the sulphur escapes

during this operation in the form of sulphurous anhydride, the residue yields the *soda-ash*, or alkali of commerce, which contains about 56 per cent. of alkali, Na_2O, reckoned in the anhydrous state. At the present time, however, the sodic hydrate which the crude liquor contains is not usually converted into carbonate, but is extracted as hydrate by a process originally proposed by Mr. Gossage, and sent into the market in a solid form (620). If required in crystals, the crude carbonate is redissolved, the liquid allowed to settle, and, while hot, is run into deep pans, capable of furnishing upwards of 1000 kilos. or about a ton of crystallized carbonate. The liquid cools in the course of five or six days, and crystals of large size are formed; the mother-liquor, which is drained off by withdrawing a plug in the bottom, is evaporated down, and yields an ash of inferior quality.

The preparation of the commercial carbonate of soda by this method, therefore, comprises three principal operations:

1st. The production of *salt-cake*, or crude sodic sulphate, from common salt, by the action of sulphuric acid.

2nd. The making of *black-ash*, or impure sodic carbonate, mixed with calcic sulphide, by deoxidation of the salt-cake after mixture with chalk, by means of carbon.

3rd. The preparation of *soda-ash*, or the separation of the sodic carbonate from the black-ash by lixiviating the latter in warm water and evaporating the solution to dryness.

Of these operations the most remarkable is the preparation of the black-ash, by fusion of the sulphate with chalk and coal. The chemical changes which occur consist, first, in the deoxidation of the salt-cake, and its conversion into disodic sulphide with evolution of carbonic oxide; and, secondly, in the formation of sodic carbonate and calcic sulphide by interchange of the constituents of the disodic sulphide and calcic carbonate. These reactions occur simultaneously, and may be represented by the following equation:

$$Na_2SO_4 + 4C + CaCO_3 = CaS + 4CO + Na_2CO_3.$$

An excess both of coal and of chalk is always employed in practice, as a good deal of coal burns off unavoidably, and an excess of chalk is needed to prevent the formation of a polysulphide of calcium. This chalk becomes quicklime in the furnace, and when the ball is lixiviated, the hydrate of lime at first produced is converted into carbonate, whilst caustic soda is formed in equivalent quantity (Gossage).

Many attempts have been made to recover the sulphur from the soda waste, the most successful of which consists in exposing the material in the tanks to a regulated oxidation by a current of air. This should be managed so that a mixture of calcic persulphide and thiosulphate (hyposulphite) is formed in such proportion that after dissolving them out from the sparingly soluble calcic hydrate and carbonate, the addition of hydrochloric acid to the solution causes the precipitation of the whole of the sulphur present in the free state; the reactions may be thus represented:

$$(1)\quad 12CaS+6O_2=2CaS_5+CaS_2O_3+9CaO$$
$$(2)\quad 2CaS_5+CaS_2O_3+6HCl=3CaCl_2+3OH_2+6S_2;$$

in practice the quantity of sulphur obtained is far less than the equations indicate, some sulphate and thionic compounds apparently being formed (905 note). In P.W. Hofmann's process, instead of employing ordinary hydrochloric acid, the excess of hydrochloric acid contained in the waste manganese liquors from the preparation of bleaching powder is utilized. The clear liquor after the subsidence of the sulphur is then worked up for the preparation of manganese compounds.

Various processes for obtaining sodic carbonate have, from time to time, been proposed, to supersede the one just described; and some years ago works on a considerable scale were established, in which upon a plan patented by Mr. Longmaid, by roasting iron or copper pyrites directly with sodic chloride, sodic sulphate was obtained without the preliminary manufacture of oil of vitriol, whilst chlorine was evolved. The reaction with iron pyrites may be thus represented: $4FeS_2+16NaCl+19O_2=2Fe_2O_3+8Na_2SO_4+8Cl_2$. A portion of the sulphur, however, always burns off in the form of sulphurous anhydride. By the employment of poor ores of copper and tin, it has been found possible to extract these metals with advantage from materials which would not otherwise have paid for working.

Ammonia Process.—Large quantities of sodic carbonate of great purity are now prepared by the 'ammonia process,' which is founded on the fact that when sodic chloride and hydric ammonic carbonate are mixed in solution, double decomposition ensues with formation of ammonic chloride and hydric sodic carbonate. Numerous patents have been taken out for rendering this reaction available for the purpose of manufacturing sodic carbonate, the most recent being those of M. E. Solvay in Belgium, and Mr. James Young in England. Ammonia is first passed into the solution of common salt in the requisite quantity, which is ascertained by the diminution in density of the solution caused by the absorption of the ammonia, and it is then saturated with carbonic anhydride, obtained by the decomposition of magnesic or calcic carbonate by heating it in a current of steam. The 'bicarbonate of soda,' which separates in the form of minute crystals is collected by means of a centrifugal machine, washed with a small quantity of water and dried, or else heated to convert it into carbonate, the evolved carbonic anhydride being used for the preparation of fresh bicarbonate. The ammonic chloride remaining in the mother-liquors is heated with lime to recover the ammonia, which is used over again. In order to obtain the

most advantageous results, the proportion of salt, ammonia, and water should be so adjusted that at the completion of the process a saturated solution of ammonic chloride should be left. The mechanical arrangements, which are somewhat complicated, are of great importance in this mode of manufacture, and for a detailed description of them we must refer our readers to Hofmann's *Bericht über die Entwickelung der chemischen Industrie*, ii. p. 445 *et seq.*

Pure sodic carbonate may be prepared by igniting pure hydric sodic carbonate, or sodic oxalate, and crystallizing the product.

Properties.—Sodic carbonate has a nauseous alkaline taste; it is an efflorescent salt, usually crystallizing in large transparent rhomboidal prisms, which melt in their water of crystallization, and are soluble in any proportion in hot water; they are also very soluble in cold water. The salt readily parts with its water, and subsequently melts at a red heat. If crystallized at a temperature of $-20°$ ($-4°$ F.), an unstable hydrate with $15OH_2$ may be obtained (Jacquelain). Mitscherlich has also obtained sodic carbonate crystallized with $6OH_2$. If crystallized above $34°$ ($93°{\cdot}2$ F.) the salt is deposited in forms derived from the square-*based octohedron, which contain* $5OH_2$; whilst, if crystallized *between* $70°$ *and* $80°$ ($158°$ *and* $176°$ F.), *four-sided prisms are produced, which contain only* OH_2: crystals containing $7OH_2$ and $8OH_2$ have also been obtained. Solutions of the carbonate may, according to Löwel (*Ann. Chim. Phys.*, 1851, [3], xxxiii. 382), be obtained in the condition of supersaturation, by adopting precautions similar to those mentioned when speaking of the sulphate. The carbonate exhibits a maximum solubility at $38°$ ($100°{\cdot}4$ F.); the decrease of solubility above this point, arising from the formation of the monohydrate, $Na_2CO_3.OH_2$, which is deposited when a solution saturated at $104°$ ($219°{\cdot}2$ F.), is concentrated by boiling.*

(628) **HYDRIC SODIC CARBONATE,** *Acid carbonate of sodium*, or *Bicarbonate of soda*; $NaHCO_3=84$; *Density*, 2·192.—This is obtained by saturating a strong solution of the normal carbonate with carbonic anhydride; the solid crystallized carbo-

* This hydrate is more soluble in cold than in hot water, and consequently becomes redissolved in the mother-liquor when it is allowed to cool. The supersaturated solution contains a hydrate with $7OH_2$. Löwel describes two modifications of this 7-molecule hydrate, which differ in solubility and in crystalline form: one variety, *a*, is deposited in rhombohedral crystals, if a solution saturated at the boiling-point be corked whilst boiling, and allowed to cool down to between

nate also absorbs carbonic anhydride with considerable development of heat; and as the bicarbonate is less soluble than the carbonate, this process is employed for procuring pure carbonate from the commercial crystals; for on washing the powdered bicarbonate with cold water until the washings are free from sulphates and chlorides, a pure bicarbonate is obtained. This salt is also manufactured upon a large scale by moistening the crushed crystals of sodic carbonate with water, and exposing them, upon cloths, to the depth of 2 or 3 inches (about 6 or 8 cm.), in stone or wooden boxes, to a current of gaseous carbonic anhydride: the water of crystallization is separated during the process, and the temperature rises considerably. The sesquicarbonate is first formed, and as the operation proceeds it is converted into the bicarbonate. The bicarbonate crystallizes in rectangular four-sided prisms, which require about 12 parts of water for solution at ordinary temperatures, 10° (50° F.). If its solution be heated, 4 molecules of the bicarbonate lose one of carbonic acid, and are converted into the sesquicarbonate, $4NaHCO_3 = 2Na_2CO_3.H_2CO_3 + CO_2 + OH_2$; and by continued boiling of the solution it is converted into the normal carbonate; $2NaHCO_3 = Na_2CO_3 + OH_2 + CO_2$. The dry bicarbonate does not lose carbonic anhydride at 25° (77° F.) in a vacuum, but at 100° (212° F.) in air it is almost entirely decomposed; the last traces of carbonic anhydride, however, require a temperature of 115° (239° F.) for their expulsion.

10° and 15° (50° and 59° F.), but it is redissolved on raising the temperature to 21° (69°·8 F.); and on cooling down to between 5° and 10° (41° and 50° F.), the modification *b* is deposited in square tables. If cooled below 4° (39°·2 F.), the solution gradually deposits the 10-molecule hydrate, and the condition of supersaturation ceases. The following table gives a comparative view of the quantities of the 10-molecule hydrate, and the two varieties of the 7-molecule hydrate contained in 100 parts of the saturated solutions at different temperatures:—

100 *parts of Water, when saturated, contain, of*

Temperature.		$Na_2CO_3.10OH_2$.		$Na_2CO_3.7OH_2(b)$.			$Na_2CO_3.7OH_2(a)$.		
°C.	°F.	Anhydr. salt.	Crystd. salt.	Anhydr. salt.	Crystd. with $6OH_2$ *b*.	Crystd. with $10OH_2$.	Anhydr. salt.	Crystd. with $7OH_2$ *a*.	Crystd. with $10OH_2$.
0	32	6·97	21·33	20·39	58·93	84·28	31·93	112·94	188·37
10	50	12·06	40·94	26·33	83·94	128·57	37·85	150·77	286·13
15	59	16·20	63·20	29·58	100·00	160·51	41·55	179·90	381·29
20	68	21·71	92·82	38·55	122·25	210·58	45"79	220·20	556·71
25	77	28·50	149·13	38·07	152·36	290·91			
30	86	37·24	273·64	43·45	196·93	447·93			
38	100·4	51·67	1142·17						
104	219·2	45·47	539·63						

A native *Sesquicarbonate of Sodium*,* $2Na_2CO_3.H_2CO_3.2OH_2 = 274 + 36$, which, however, always contains sodic sulphate and chloride, has been long known in commerce as *trona* or *natron*; it is chiefly obtained as a saline efflorescence on the borders of some lakes, of which those of Egypt are the best known. Many other countries, however, such as those in the neighbourhood of the Black and the Caspian seas, as well as some parts of Thibet and of Siberia, also furnish this salt. It crystallizes in rhombic prisms, terminated by four-sided pyramids; it is less soluble than the normal carbonate, but more so than the bicarbonate, and has a feebly alkaline reaction.

The normal sodic and potassic carbonates, when melted together in the proportion of 1 molecule of each ($K_2CO_3 + Na_2CO_3$), readily combine and form a salt which fuses at a lower temperature than either of its components. On account of its ready fusibility, this mixture is preferred to either carbonate alone, as a means of decomposing siliceous minerals in analytical operations (619). If sodic carbonate be dissolved in a solution of potassic carbonate in excess, the solution, on evaporation, yields transparent crystals which, according to Marignac, consist of $NaKCO_3.6OH_2$: this salt is decomposed if it be attempted to recrystallize its aqueous solution, normal sodic carbonate being deposited.

(629) **PHOSPHATES OF SODIUM.**—Phosphoric acid forms with sodium several crystallizable salts: some account has already been given of these compounds (516, 517, 518).

Trisodic Phosphate, or *Subphosphate of soda*; $Na_3PO_4.12OH_2 = 164 + 216$; *Density, cryst.* 1·618.—This salt is prepared from the rhombic phosphate by adding caustic soda to its solution until it feels soapy to the fingers. It crystallizes readily in small prisms, which effloresce in the air, and gradually absorb carbonic anhydride. A remarkable double salt of this phosphate with sodic fluoride, of the composition $NaF.Na_3PO_4.12OH_2$, was obtained by Briegleb, by fusing the rhombic or hydric disodic phosphate with fluor-spar and sodic carbonate; and also by digesting powdered cryolite with a mixture of rhombic phosphate and caustic soda.

Hydric Disodic Phosphate, or *Rhombic phosphate of sodium*; $Na_2HPO_4.12OH_2 = 142 + 216$; *Density, cryst.* 1·525; *anhydr.* 1·619.—This salt is the one from which most of the phosphates are formed: it is the one which has been longest known, and is that commonly called 'phosphate of soda.' It is best prepared by neutralizing with sodic carbonate the acid phosphate of calcium, prepared as directed for obtaining phosphorus (498): by this means tricalcic phosphate is precipitated, and allowed to subside; the

* The terms bicarbonate and sesquicarbonate are incorrect; but they are well understood, and convey with distinctness the ideas intended.

clear liquid is then decanted from the precipitate, evaporated if necessary, and set aside to crystallize. Hydric disodic phosphate forms large, transparent, efflorescent rhombic prisms: they have a cooling saline taste, and are soluble in 4 parts of cold water; at 37°·2 (99° F.) they fuse in their water of crystallization, and are therefore soluble in boiling water to an unlimited extent; the solution has a faintly alkaline reaction. When carbonic anhydride is passed into a dilute solution of the salt, it is converted into dihydric sodic phosphate, $Na_2HPO_4+CO_2+OH_2$ becoming $NaH_2PO_4+NaHCO_3$. It corrodes flint-glass bottles, and occasions the separation of white siliceous flakes from their surface. Clark found that when the solution of this salt is evaporated at temperatures above 32°·2 (90° F.) the salt crystallizes with 7 molecules of water, and is not efflorescent; in both forms it is isomorphous with the corresponding hydric disodic arseniate. If heated at 150° (302° F.) it loses all its water of crystallization; but if redissolved in water it may be obtained from its solution with all its characteristic properties. If a solution of this phosphate be mixed with free phosphoric acid, until it ceases to precipitate baric chloride, another phosphate is produced, *the sodic dihydric phosphate*, formerly known as *biphosphate of soda*, $NaH_2PO_4.OH_2=120+18$; it crystallizes with difficulty in right rhombic prisms, and has a strongly acid reaction.

All these are tribasic phosphates; they precipitate argentic nitrate of a yellow colour.

Tetrasodic Phosphate, or *Pyrophosphate of sodium*; $Na_4P_2O_7.10OH_2=266+180$; *Density. cryst.* 1·836.—If the rhombic phosphate be ignited it loses all its water, and on then treating it with water, a new tetrabasic salt is dissolved, which crystallizes in prisms. Its solution has an alkaline reaction, and with argentic nitrate, yields a dense white precipitate which is not changed by exposure to light.

Sodic Metaphosphate, or *Metaphosphate of sodium*; $NaPO_3=102$.—If microcosmic salt, or if the sodic dihydric (acid tribasic) phosphate, or the dihydric disodic pyrophosphate (acid pyrophosphate), be heated to redness, all the volatile bases are expelled, the residue fuses to a clear glass, and on redissolving, sodic metaphosphate or monobasic phosphate of sodium is obtained. It forms a deliquescent and very soluble salt, which has a feebly acid reaction upon litmus. It cannot be obtained in crystals. The solution of this salt causes, with argentic nitrate, a white gelatinous precipitate, soluble in excess of the metaphosphate; with

baric or calcic nitrate a similar gelatinous precipitate is formed. This salt is susceptible of various modifications by the application of different temperatures (518).

(630) **BORAX**, *Acid borate of sodium*, or *Sodic pyroborate*; $Na_2B_4O_7.10OH_2 = 202 + 180$; *Density, fused*, 2·367, *cryst.* 1·73; *Comp. in* 100 *parts, anhydr.*, Na_2O, 30·69; B_2O_3, 69·31; *cryst.* Na_2O, 16·23; B_2O_3, 36·65; OH_2, 47·12.—This well-known salt is produced in considerable quantities in various parts of the world, particularly in Thibet, whence for many years the principal part of the borax consumed was supplied. The crude borax, or *tincal*, is obtained by the spontaneous evaporation of the waters of the lakes whence it is derived, and occurs crystallized in flattened six-sided prisms, terminated by trihedral summits. These crystals are, however, very impure, being covered with a greasy coating, said to be derived from the skins in which they are imported. In order to remove this grease, the crystals are powdered, thrown upon a filter, and washed with a weak solution of caustic soda, which forms a soap with the grease, and dissolves it; the remaining salt is dissolved in water. Sodic carbonate equal to one-eighth of the weight of the borax is added to the solution: a copious precipitate of earthy impurities ensues, the liquid is cleared by filtration, and allowed to cool very slowly: the borax is deposited in rectangular or in six-sided prisms, containing $10OH_2$, one molecule of which is probably basic.

A large quantity of borax is now manufactured from the boric acid obtained from the lagoons of Tuscany, by saturating it with sodic carbonate, and allowing the salt to crystallize. In the course of this operation the crude boric acid is mixed with about half its weight of soda-ash, and is thrown, in quantities of about 3 cwt. at a time, upon the floor of a reverberatory furnace; the mixture soon frits and effervesces, and must be well stirred during the process: a quantity of carbonic anhydride, of ammonia, and of organic matter which always accompanies the boracic acid, is got rid of in this operation.* The fritted mass is then lixiviated in deep iron boilers. Here the solution is allowed to remain at rest, in order that the impurities, which consist chiefly of alumina, calcic carbonate, and some silica, may subside; and the liquid, when brought to the density of 1·166, is drawn off into wooden tanks lined with lead, where the solution

* The ammonia which is lost by operating in this manner is in some works economized by dissolving sodic carbonate in water in tanks, adding the acid gradually, and conducting the vapours from the hot liquid into a reservoir containing sulphuric acid.

cools very slowly. It is also prepared from boronatrocalcite (724), when it is tolerably pure and free from gypsum, by simply digesting it with a solution of soda in quantity sufficient to decompose the calcic borate present, and then evaporating the clear solution to the crystallizing point. The large crystals in which borax is demanded for the market can be procured only by operating on very large masses of the salt, and allowing it to crystallize from a solution containing sodic carbonate in excess. Borax may also be obtained in octohedral crystals* ($NaH_2BO_3.2OH_2$; density, 1·815), if the salt be allowed to crystallize at a temperature between 80° and 55° (176° and 131° F.), from a solution of density 1·246, to which about one-third more of sodic carbonate is added than is required to form the salt.

Borax is the normal sodic salt of pyroboric acid; it has a feebly alkaline taste and reaction. The prismatic crystals are soluble in about half their weight of boiling water, and in 12 parts of cold water; they are slightly efflorescent. When heated, borax intumesces, loses its water, and melts below redness to a transparent glass: this glass dissolves many metallic oxides, which often impart intense and characteristic colours to the bead, so that borax is much used as a blowpipe test for recognizing the presence of these oxides. For this purpose a small crystal of borax is fused upon the end of a bent platinum wire, and a minute quantity of the substance to be tested is melted with the salt in the flame of the blowpipe: the colour of the glass varies according as the bead is heated in the oxidizing or in the reducing flame (380). The power which this salt possesses of dissolving the metallic oxides renders it useful in the process of soldering oxidizable metals which require a high temperature, the metallic surfaces being sprinkled with powdered borax; on the application of heat, the borax melts as well as the solder, and the film of oxide which would otherwise prevent the adhesion is removed from the pieces of metal at the moment that the alloy is presented to unite them. Borax is used in the arts as a flux, and by the refiner in the melting of gold and silver. In making enamels, it is frequently added for the purpose of rendering the compound more fusible, and it is also largely employed in fixing colours on porcelain.

Other borates of sodium may be formed, but ordinary borax

* These crystals have been recently examined by Arzruni, who finds that they are not octohedral, but belong to the hexagonal system.

is the only salt of any practical importance; the tetraborate, $2(NaBO_2.3HBO_2).7OH_2$, crystallizes with great difficulty: a *normal metaborate* may be obtained by fusing 1 molecule of ordinary borax with 1 of sodic carbonate; it crystallizes in oblique, rhombic prisms, $NaBO_2.4OH_2$. These absorb carbonic anhydride from the air.

(631) **SILICATES OF SODIUM.**—When finely divided silica is gradually added to fused sodic carbonate, carbonic anhydride is evolved with effervescence, and a mixture of various silicates of sodium is formed. Fritsche obtained a silicate of the composition, $Na_2O.SiO_2.9OH_2$, by dissolving in a strong solution of caustic soda a quantity of silica equal in weight to the anhydrous soda present in the liquid: it crystallizes sometimes with 6, sometimes with 9, molecules of water. This silicate may also be obtained by fusing 2 parts of powdered flints with 3 of sodic carbonate. When a concentrated solution of sodic carbonate is boiled with finely divided silica, a large proportion of silica is dissolved: but the clear liquid, as it cools, deposits a gelatinous precipitate, consisting, according to Forchhammer, of $Na_2O.36SiO_2$. Other silicates have been obtained, to which the proportions indicated by the formulæ $2Na_2O.5SiO_2$; $Na_2O.3SiO_2$ and $Na_2O.4SiO_2$ have been assigned. It is difficult, however, to prove the existence of these compounds with the exception of the one last named. The silicate, $Na_2O.SiO_2$, has the property of being dissolved by an excess of fused sodic carbonate, and the glass, which is clear and transparent whilst hot, becomes opaque on cooling; but the same silicate, if heated sufficiently with an excess of silica, melts and forms a homogeneous mixture, which yields a transparent glass on cooling, the fusibility decreasing as the proportion of silica increases, until, when the quantity of silica amounts to 9 molecules, the heat of a forge is required to melt it. The silicates are all more or less soluble in boiling water.

A peculiar silicate, represented by the formula $Na_2O.4SiO_2$, which has received the name of *soluble glass*, is prepared by melting together 8 parts of sodic carbonate (or 10 of potassic carbonate), with 15 of pure quartz sand and 1 part of charcoal (Fuchs): the charcoal by its tendency to form carbonic oxide at the expense of the oxygen of the carbonate, facilitates the decomposition of this salt: a black glass is thus obtained, which is not soluble in cold water, but is almost completely dissolved by 5 or 6 times its weight of boiling water: this solution gives a voluminous gelatinous precipitate consisting of unaltered water glass,

$Na_2O.4SiO_2$, on adding to it ammonia, sodic nitrate, and many other salts. The precipitation by ammonia may be utilized for preparing the pure silicate. Soluble glass is employed in fixing fresco colours, by the process known as *stereochromy*. The ground employed in this process for the reception of the colour consists of a mixture of lime and fine sand, cemented by a solution of soluble glass. The colours, ground up with water, are then applied, and a varnish of soluble glass is brushed over the whole. The material best adapted to this purpose consists of a mixture of this soluble glass solution with about one-fifth of its bulk of a solution of the monosilicate, both solutions being in a concentrated state (Fuchs).

Many metallic oxides—such as lime, magnesia, and zincic oxide, and their salts—are, as Kuhlmann has shown, acted upon by the solution of sodic silicate; calcic carbonate and other salts being converted by it into masses of great hardness and durability; double decomposition of the silicate and earthy salt occurring to a greater or less extent. By a further extension of this principle, Mr. Ransome has applied a solution of potassic or sodic silicate to the prevention of the decay of magnesian and other limestones which are exposed to the weather: a solution of the silicate is brushed over the surface of the stonework, and this is followed up by washing the stone over, when dry, with a solution of chloride of calcium, double decomposition occurs within the pores of the stone, the soluble chloride of sodium is formed, and may be removed by washing, whilst the surface becomes converted into the insoluble calcic silicate.

A very hard artificial sandstone is now also prepared by mixing sand with a solution of calcic chloride, pressing it in a mould of the desired form, and then decomposing the calcic salt by silicate of soda, added in suitable proportions; the solution of silicate is forced into the mass by atmospheric pressure, and the sodic chloride is then washed out, water being also forced through the stone by atmospheric pressure.

A solution of sodic silicate as nearly neutral as possible is now very generally used as a substitute for cow-dung in preparing mordanted calico for dyeing. This constitutes one of the most important applications of the salt. This solution may be obtained of a density of 1·53. It may be prepared either by fusing silica with sodic carbonate in the proper proportions, or by digesting calcined flints under pressure in a concentrated solution of caustic soda.

When heat is applied to the silicates of the alkalies, they do not at once become liquid, but pass through an intermediate viscous stage; they impart this viscidity, and the transparency

which they preserve on cooling, to many other silicates if they are fused with them, and they destroy the tendency to crystallize which the silicates of the earths and of the heavy metallic oxides possess. This property is of the highest importance to mankind, for upon it depend the most valuable properties of glass—ductility, which enables it to be moulded whilst in this intermediate state, and transparency, which renders it applicable to a multitude of important uses. The silicates of the alkalies are unable alone to resist the action of water and other solvents sufficiently to fit them for many of the applications of glass; but when combined with silicates of the earths and certain metallic oxides, mixtures may be obtained which are no longer soluble in water or in acids.

(632) **GLASS.**—The composition of glass differs considerably with the nature of the purposes to which it is destined, but it consists mainly of mixtures, in varying proportions, of silicates of potassium, sodium, calcium, barium, magnesium, aluminium, and lead, coloured by the addition of small quantities of different metallic oxides, particularly those of iron, manganese, cobalt, copper, uranium, and gold.

The degree of fusibility of these different silicates varies greatly. The calcic and magnesic silicates fuse with great difficulty when heated *per se*: the most fusible compound contains 2 molecules of base to 3 of silica, the quantity of oxygen in the base, being to that in the silica as 1 is to 3. The ferrous sesquisilicate, $2FeO.3SiO_2$, and manganous sesquisilicate, are readily fused, and crystallize on cooling. Plumbic sesquisilicate, $2PbO.3SiO_2$, is still more fusible, and on cooling forms a yellow transparent glass. On the other hand, aluminic disilicate, $Al_2O_3.2SiO_2$, is nearly infusible in the furnace. All these silicates, however, when mixed with each other, or with the silicates of the alkalies, melt at considerably lower temperatures, the fusing-point being generally much below that of the mean of the different silicates employed. The calcic and aluminic silicates are nearly infusible when separate, but they melt readily after they have been mixed together.

Most of the properties of glass are familiar to every one. It is a transparent brittle solid, more or less fusible, and just before it melts is possessed of remarkable ductility, a property which enables the workman to fashion it into the numberless forms which luxury or convenience dictates. The different varieties of glass are not to be regarded as definite compounds, but as mixtures of various silicates in different proportions, with an excess

of silica. It is generally found, however, in the best kinds of glass, that the mixtures are very nearly in such proportions that but little silica remains in the uncombined form. The proportion of silica to the bases is most conveniently expressed by ascertaining the proportion which the oxygen of the bases bears to that of the silica. The subjoined table gives the result of some analyses of the more important kinds of glass:

Composition of different Varieties of Glass in 100 *parts.*

	Dumas.		Richardson.	Dumas.	Berthier.	Rowney.
	Bottle.	Window.		Plate.		Glass tube.
	French.	French. soft.	English.	French.	Venetian.	Bohemian.
Silica	53·55	69·65	66·37	73·85	68·6	73·13
Potash	5·48	...	...	5·50	6·9	11·49
Soda	...	15·22	14·23	12·05	8·1	3·07
Lime	29·22	13·31	11·86	5·60	11·0	10·43
Magnesia ...	...	...	...	...	2·1	0·26
Alumina ...	6·01	1·82	8·16	3·50	1·2	0·30
Oxide of iron ...	5·74	...	...	...	0·2	0·13
Oxide of manganese ...	...	...	...	...	0·1	0·46
Ratio of the oxygen in the bases to that in the silica	1 : 2	1 : 4	2 : 7	1 : 6	1 : 5	1 : 6

	Dumas.		Faraday.	Dumas.		
	Bohemian goblet.	German crown.	English flint.	Guinand's optical.	Strass.	Enamel.
Silica	69·4	62·8	51·93	42·5	38·1	31·6
Potash	11·8	22·1	13·77	11·7	7·9	8·3
Lime	9·2	12·5	...	0·5	...	
Alumina ...	9·6	2·6	0·47	1·8	1·0	
Oxide of lead ...	...	...	33·28	43·5	53·0	50·3
Oxide of tin ...	...	...	...	...	...	9·8
Oxides of iron and manganese ...	...	...	0·27	...	As_2O_3, B_2O_3 } trace.	
Ratio of the oxygen in the bases to that in the silica.	1 : 4	1 : 5	1 : 6	1 : 4	1 : 4	3 : 7

(633) **Bohemian Glass,** or *Glass in which Potassic and Calcic Silicates predominate.*—The potassic and calcic silicates are the principal components of the celebrated Bohemian glass, including the variety which is employed in the preparation of the hard

glass of difficult fusibility, so much prized in the laboratory for the tubes used for the combustion of organic compounds: the composition of this glass, according to Dumas, may be represented approximatively by the formula $K_2O.3SiO_2 + CaO.3SiO_2$, part of the potassium having its place supplied by sodium, and part of the calcium by magnesium, aluminium, and traces of iron and manganese: according to Benrath, however, the formula of 'normal glass' is $5\ [(NaK)_2O.3SiO_2] + 7CaO.3SiO_2$, ordinary glass being mixtures of this with a slight excess of alkaline silicate to render it more fusible. The more fusible glass which is employed in the manufacture of the beautiful ornamental objects for which Bohemia has long been distinguished, contains aluminic silicate, with potassic and calcic silicates, in a proportion which approaches $3(KCa)O.Al_2O_3.12SiO_2$. The crown glass employed for optical purposes has nearly the formula $K_2O.CaO.4SiO_2$ (Dumas, *Ann. Chim. Phys.*, 1855, [2], xliv. 151). In the last two cases the proportion of oxygen in the bases to that in the silica is very nearly as 1 : 4.

In the finer kinds of glass, potash is always employed in preference to soda, because the glass made from soda, however carefully the materials are selected, has a bluish-green tinge, which is not observed when potash is used. The potash glass, however, is rather less brilliant than that which contains soda.

(634) **Plate and Window Glass,** or *Glass consisting of Sodic and Calcic Silicates.*—French plate glass and ordinary window glass are the most important varieties of this description. Plate glass is very fusible, although the oxygen of the bases which it contains amounts only to about one-sixth of that of the silica. Soda produces a more liquid and fusible compound than potash. The addition of lime to glass diminishes its fusibility, whilst it increases its lustre and hardness without affecting the colour. Care must be taken not to employ an excess of lime, for it is liable to render the glass milky-looking on cooling, although it may be perfectly transparent whilst hot.

Great care is required in the selection of the materials employed in the manufacture of the finer kinds of glass. The ingredients used in the plate glass of St. Gobain consist of 300 parts of white quartzose sand, 100 of dry sodic carbonate, 43 of lime, slaked by exposure to the air, and 300 of fragments of broken glass from previous meltings. The fuel employed in the furnace is wood.

These materials are intimately mixed, and then melted in a large, deep, conical crucible, in which, after they have been com-

pletely fused, they are allowed to stand at a high temperature for several hours, in order that the impurities may subside. Quantities of this mixture sufficient for casting a single sheet are then removed, by means of copper ladles, into a smaller square crucible, termed the *cuvette.** When the glass is thoroughly melted, the cuvette is removed from the furnace by a crane, and the glass is cast by pouring it upon a solid table of cast-iron; along the edge of this table are ledges of metal, to regulate the thickness of the sheet of glass, and the molten mass is immediately spread and formed into a plate by means of a heavy, hollow metallic roller. These sheets are next annealed by being placed in a heated oven, and allowed to cool very slowly down to the temperature of the air—an operation which requires from a week to a fortnight for its completion. They are then levelled by cementing one plate with plaster of Paris upon a slab, and causing a second plate to move, by machinery, over the surface of the first, the grinding material being fine sand and water: a level surface having been thus obtained, it is smoothed by emery of gradually increasing fineness, and the final polish is given by friction with finely levigated colcothar or ferric oxide.

Window glass is made of a mixture of 100 parts of sand, with from 35 to 40 of chalk, 30 to 35 of soda ash, and from 50 to 150 of broken glass, or *cullet.* An equivalent amount of the cheaper sodic sulphate may be substituted in this mixture for the carbonate, for at a very elevated temperature the silica expels the elements of sulphuric anhydride; this decomposition may be facilitated by mixing the sulphate with about a tenth of its weight of charcoal; the sulphate is thus reduced to a lower state of oxidation, and the sulphur escapes in the form of sulphurous anhydride at a lower temperature than that required to decompose the sulphate.

When sodic carbonate is used, the materials are first subjected to a heat insufficient to completely fuse the mass, and are *fritted* together, or heated until they agglomerate; moisture is thus completely expelled, and a part of the gaseous carbonic anhydride is got rid of: the frothing up of the mixture in the subsequent fusion, due to the expulsion of the gas, is also diminished, and the loss of alkali by volatilization is considerably lessened. The fritted mass is then transferred to other pots, and the temperature

* In the Thames Plate-glass Works, the glass is melted in the same pot as that from which it is poured in casting. The pots are cylindrical, and the fuel employed is coal.

of the furnace is raised until complete fusion is effected. The mixture, after it has been thoroughly melted, is allowed to stand, in order that the bubbles of air may escape, and that the mass may become uniform in composition: the excess of sulphate or of chloride of sodium which may have escaped decomposition rises to the surface and is skimmed off, forming what the manufacturer terms *glass-gall* or *sandiver*. The glass is then allowed to cool until it assumes the pasty, tenacious condition required for the manipulations of the glass-blower.

(635) **Bottle Glass**, or *Glass containing Silicates of Aluminium, Calcium, Iron, Magnesium, and Sodium or Potassium.*—The inferior descriptions of glass which are used for making wine-bottles, carboys, and other articles in which a dark colour is unimportant, consist of a mixture of these silicates. The materials employed are of a coarser kind than those used in the preceding varieties of glass. A ferruginous or ochry sand, mixed with soap-maker's waste, are common ingredients. Mr. Pellat gives the following as a composition employed in making bottle glass:—Sand, 100 measures; soap-maker's waste, 80; gas-lime, 80; common clay, 5; and rock-salt 5 measures. The ordinary English bottles are of an olive-green colour, produced by the presence of magnetic oxide of iron; whilst some of the German bottles are of a pale brown, resulting from a mixture of the oxides of iron and manganese. Sometimes baric sulphate is added with the view of rendering the glass more fusible. Bottle glass contains a smaller proportion of silica than any of the preceding varieties. One specimen analysed by Dumas, presented a composition which would be approximatively represented by the formula $6(CaK)O.(AlFe)_2O_3.9SiO_2$; whilst in a second specimen the composition would be more nearly represented by $6(CaK)O.2(AlFe)_2O_3.9SiO_2$. The oxygen of the bases, in the first instance, is in the proportion to that of the silica as 1 to 2, and in the second case nearly as 2 to 3.

(636) **Devitrification; Reaumur's Porcelain.**—Bottle glass is particularly liable to become devitrified by slow cooling, and to be converted into what is termed *Réaumur's Porcelain*. In order to produce this effect, the glass may be imbedded in sand, or, still better, in a mixture of gypsum and sand, and heated up to a point sufficient to soften it, but just short of that required for its fusion: in this way, bottle glass readily becomes devitrified on heating it in chalk or powdered coke for an hour and a half, and glass containing magnesia is also devitrified. If it be now allowed to cool very slowly, it will be found to have entirely altered its aspect and properties; having become opaque and milk-white, and much resembling porcelain in appearance. It is now somewhat less fusible, and less liable to crack on the application of sudden changes of temperature, and is much harder than the glass from which it was procured. It

is a bad conductor of heat, but conducts electricity to a considerable extent, being comparable in this respect to marble (Pelouze). This alteration appears to be due to the partial separation of certain silicates, particularly of the calcic and aluminic silicates, and their assumption of a more or less definite crystalline form. This crystallization is sometimes very beautifully and perfectly exhibited in the residues at the bottom of the glass-pots, which are allowed to cool down with great slowness and regularity. Nodules of opaque radiated crystals are there often found surrounded by a transparent glass. A mass of these opaque crystals, analysed by Dumas, presented a composition which corresponded with the formula $18(CaNa)O.2Al_2O_3.45SiO_2$; whilst the transparent glass from which they had separated contained 3·5 per cent. less of silica, 1·4 less alumina, and a proportionately larger quantity of soda. Some crystals resembling pyroxene in form, deposited from bottle glass, have also been analysed by Peligot (*Compt. Rend.*, 1874, lxxviii. 386): they differed but little in composition from the molten transparent glass, which confirms the results obtained by Benrath (*Ding. Poly. Jour.*, 1872, cciii. 19).

The devitrification of glass has been made the subject of experiment by Pelouze (*Chem. Gaz.*, Aug. 1855). He finds that the same sheet of glass may be devitrified, and again rendered transparent by fusion, many times in succession. Glass of any description may be devitrified, but the finer kinds of potash-glass exhibit this phenomenon with difficulty. The throwing in of a small quantity of sand, or even of powdered glass, into a pot after it has cooled down to the viscid condition, greatly promotes the devitrification of the mass. The soluble soda-glass of Fuchs, $Na_2O.4SiO_2$, is especially liable to devitrification from crystallization.

(637) **Flint Glass**, or *Glass containing Silicates of Potassium and Lead.*—The ordinary white glass in use in this country, commonly known as flint glass (the *cristal* of French writers), consists almost entirely of these silicates. Potash is used instead of soda in the preparation of flint glass, in order to avoid the bluish tint which is produced by soda in combination with oxide of lead. The oxide of lead imparts a greater degree of fusibility and density, as well as a high refractive and dispersive power; in consequence of which such glass, from its superior brilliancy, is better fitted for the manufacture of ornamental articles, and from its greater softness is more easily cut and polished. Lead glass has, however, the inconvenience of being readily scratched, and it is liable to tarnish and change colour, especially if the proportion of alkali be large. The alkalies corrode it slowly, and it becomes gradually blackened when left in contact with solutions of the sulphides. According to Faraday's experiments, English flint glass contains one-third or more of its weight of oxide of lead: it may be represented very nearly by the formula $K_2O.PbO.6SiO_2$. But in a specimen from Newcastle, examined by Berthier, the proportion of silicate of lead was larger: this glass corresponded nearly to the formula $2K_2O.3PbO.15SiO_2$. The composition of flint glass, however, is liable to considerable variation, even in different parts of the same pot, the lower por-

tions having generally a greater density than those in the upper part of the pot. This arises from the density of the oxide of lead being much greater than that of the other materials, so that it is extremely difficult to preserve a uniform mixture. Faraday found, for example, that glass taken from the top of pots not more than 15 cm., or six inches deep, might have a density of 3·28, whilst that from the bottom might have a density of 3·85: in one instance the glass at the top had a density of 3·81, that at the bottom of 4·75; and although these are extreme differences, there is no doubt that considerable variations occur in every pot of glass made in the usual way. This variation in the density of the glass occasions great inconvenience in its application to the construction of optical instruments, owing to the difference of its refracting power in different portions of the same mass; and many endeavours have been made to overcome these defects. A lead glass of still higher refracting power was made by Guinand, in which the proportion of lead was very large, the formula being very nearly $2K_2O.3PbO.10SiO_2$, the proportion of oxygen in the bases being to that in the silica as 1 to 4: its specific gravity was 3·61. Faraday (*Phil. Trans.*, 1830, p. 42) proposed, for a similar purpose, a compound of plumbic silicate and borate, the density of which is 5·44: this glass has a pale lemon-yellow tint, and consists of $3(PbO.SiO_2)+3PbO.2B_2O_3$. Of late years a zincic borosilicate has been introduced by Maez and Clemandot into the glass used for optical purposes, with considerable success.

Much of the success in the preparation of glass for optical purposes depends upon the selection of pure materials, and also on their complete incorporation. The plan which succeeds best in attaining the latter object was introduced by Guinand. After the fusion is complete, the melted glass is thoroughly stirred with a paddle of crucible clay; the crucible and its contents are then allowed to cool down slowly in the furnace; when cold, the pot is broken, and by means of a wire and sand, kept wet, the mass of glass is cut *horizontally* into slices; in this way pieces of uniform density may generally be obtained. A good optical glass may be made from a mixture of 100 parts of pure sand, 100 of minium, and 30 of refined pearlash.

The oxide of lead which is employed in the manufacture of flint glass is not ordinary litharge (1069), but minium or red lead (1070), which is a higher oxide of lead, and is prepared with care from pure lead. The proportions of the materials usually employed in the manufacture of flint glass are, 300 of fine white sand, such

as that from Lynn on the coast of Norfolk, or from Fontainebleau, 200 of minium, and 100 of refined pearlash, with about 30 parts of nitre. In all cases the selection of materials for the melting-pot is of high importance. These pots are best made of an infusible clay, such as that from Stourbridge, which contains but little lime and iron: 5 parts of clay and 1 part of ground-burnt pots are trodden into a mass by the workman, and allowed to stand for three or four months: the mixture is then carefully wrought into pots about four inches (10 cm.) thick, great care being taken to exclude air-bubbles. The pots are allowed to dry for several months in a warm room, after which they are removed to an annealing oven, where they are raised very gradually to the temperature of the furnace. Flint glass is always made in pots which are arched over at top, and have an opening at the upper part of one side for the introduction of the charge and the withdrawal of the glass: they are set in the furnace in such a manner as to prevent the access of smoke and combustible gases to the interior, which would endanger the reduction of the oxide of lead to the metallic state. Plate glass, crown glass, and the other varieties of glass, are made in open crucibles. The alumina, which is contained even in the finest glass, is chiefly derived from the action of the vitrified materials upon the clay of the pots.

(638) **Coloured Glasses—Enamel.**—For the purpose of producing imitations of precious gems, a lead glass of still higher refracting power, termed *paste* or *strass*, is employed, the proportion of oxide of lead exceeding 53 per cent.; the composition of this substance is very nearly represented by the formula, $K_2O.3PbO.8SiO_2$, the proportion of oxygen in the bases being one-fourth of that present in the silica. A little borax is often added to this glass to increase its fusibility. Glass of this description, when properly cut, is employed to imitate the diamond. The yellow colour of topaz is given to the strass by the addition of about 1 per cent. of ferric oxide, or by a mixture of 4 per cent. of antimonious oxide with a minute proportion (0·1 per cent.) of purple of Cassius. The brilliant blue of sapphire is imitated by adding a small quantity of cobalt oxide.

It is, indeed, a property of glass to dissolve small quantities of many of the metallic oxides without losing its transparency; the glass becoming coloured with more or less intensity, and with different hues, according to the nature of the metallic oxide employed. Ferrous oxide appears to pass into the condition of magnetic oxide, which even in small quantities is able to communicate colour, varying from a pale green to a deep bottle-green,

according to the proportion in which it is present: ferric oxide, on the contrary, although it has but feeble colouring power, is capable of producing a yellow colour when present in considerable quantity; manganous oxide is nearly colourless, but the sesquioxide communicates a violet tint to the glass. Advantage is taken of the knowledge of these facts in preparing colourless glass: ferrous oxide, in minute quantity, is a frequent impurity in the materials used, and it produces the green tinge often observed in ordinary glass: a minute quantity of black oxide of manganese corrects this; it imparts oxygen to the magnetic oxide of iron, which thus becomes converted into the colourless sesquioxide, whilst the manganese itself being reduced to the state of protoxide, exerts no injurious colouring effect. A little nitre or arsenious anhydride is sometimes added to glass instead of oxide of manganese, with a similar effect in converting the iron into sesquioxide. The manganese is, however, the more effectual agent; this may arise, as Liebig suggests, from the circumstance that the colours produced by the iron and manganese are each complementary to the other. Chromic oxide imparts an emerald-green tinge to glass; cobalt oxide a deep blue. A mixture of the oxides of cobalt and manganese gives a black glass; cupric oxide, CuO, produces a green; cuprous oxide, Cu_2O, an intense ruby red; whilst the sparkling appearance of avanturine may be imitated by the dissemination of tetrahedral crystals of reduced metallic copper through the mass. Uranic oxide communicates to the glass a peculiar opalescent yellow; different shades of yellow are also produced by oxides of silver and antimony, and by finely divided charcoal; and a compound of gold with oxide of tin (purple of Cassius) gives a magnificent ruby glass.

Sometimes glass is *flashed*, or superficially coated with the coloured portion. A mass of colourless glass is in this case taken by the workman upon the end of his blowing tube, and then dipped into a pot of the coloured glass—ruby, blue, or opal, as the case may be; on blowing out the lump of glass, a vessel is obtained, the exterior layer of which is coloured, whilst the inner layer consists of colourless glass.

Painting on glass is effected by means of a very fusible glass, which when melted gives the required tint; this glass is reduced to a very fine powder, and worked up with turpentine into a pigment: it is then applied with a hair pencil to the surface of a sheet of ordinary glass. The painted glass is afterwards subjected to a heat which is sufficient to melt the coloured glass, but is not intense enough to soften the glass to which it is applied.

Enamel is the term given to an easily fusible glass, through which is disseminated an opaque white substance infusible at the temperature employed, such for example as the stannic oxide; a metallic ash is prepared by calcining at a low red heat a mixture of 1 part of tin with from 1 to 6 parts of lead, in a flat cast-iron vessel; the ash so obtained is mixed with sand and alkali, the proportions of which may vary considerably. In one recipe for the preparation of enamel given by Knapp, the ashes of 4 parts of tin and 10 of lead are directed to be ground up with 10 parts of powdered quartz and 2 of pure soda-ash. Other opaque bodies may be substituted for the stannic oxide in the preparation of enamel: in this manner bone-ash, antimonious oxide, and even arsenious anhydride, are sometimes employed to produce the opacity required. The enamel may be tinged of any desired colour by the suitable addition of metallic oxides. The enamel is applied with a brush to the surface to which it is to be attached, and is then fused by exposure to heat.

A modification of glass resembling enamel has been used to glaze cast-iron pots, as a substitute for tinning. It consists of powdered flints ground with calcined borax, fine clay, and a little felspar. This mixture is made into a paste with water, and brushed over the pots, after they have been scoured with dilute sulphuric acid and well rinsed with water; while they are still moist, they are dusted over with a glaze composed of felspar, soda-ash, borax, and a little stannic oxide. Having been thus prepared, the pots are next carefully dried, and finally the glaze is fused or *fired* under a muffle at a bright red heat. Plumbic oxide, although it increases the fusibility of the glaze, should be carefully avoided, as it does not resist the action of acids in culinary operations.

(639) **Properties of Glass.**—Well-made glass is not perceptibly acted upon by any acid or mixture of acids except hydrofluoric, which destroys it by combining with its silica. But it is not absolutely insoluble, although it is generally considered to be capable of withstanding the action of water. If glass be powdered and moistened with water, the liquid will dissolve a small quantity of alkali, sufficient to turn turmeric-paper brown. Most varieties of glass when powdered and exposed for some time to the air, were found by Pelouze to absorb carbonic anhydride in quantity sufficient to effervesce when treated with an acid, particularly if they had been kept moistened with water. If left long in water, or buried in moist earth, many kinds of glass become disintegrated slowly, and scale off in flakes which exhibit the brilliant colours of Newton's rings (116). This is particularly the case with the coarse glass used for wine bottles. Faraday found that some inferior kinds of bottle glass were destroyed rapidly by the action of dilute sulphuric acid.

At a high temperature water gradually decomposes glass; pieces of plate and window glass were suspended by Turner in the steam of a high-pressure boiler, and in the course of four months, specimens of plate glass one-fifth of an inch ($5^{mm.}$) thick were completely decomposed; and Faraday found that flint glass, under similar circumstances, was still more rapidly acted upon.

(640) **Hardened Glass.**—If glass be suddenly cooled after fusion, it becomes extremely brittle; and a similar change takes place when glass articles are allowed to cool rapidly by exposing them whilst red hot to the external air. Glass objects of this description, if their surface be but scratched, or if they be brought suddenly from a cold room into a warm one, will often crack and fall to pieces. In order to prevent this mishap, it is necessary to subject the different articles, after they have received their destined shape at the hands of the workman, to the operation of annealing, which is a very slow and gradual process of cooling; the parts are thus enabled to assume their natural position with regard to each other. Even then, since glass dilates considerably on the application of heat, and is likewise a bad conductor, a sudden and incautious elevation of temperature, such as that occasioned by pouring boiling water into a cold glass, often causes its fracture. Care is required during the process of annealing, especially with the coarser kinds of glass, not to raise the temperature too high, as otherwise devitrification to a greater or less extent would be liable to ensue.

When drops of melted glass are allowed to fall into water, they solidify in pear-shaped masses, which do not break even when subjected to considerable pressure if it be gradually applied; but if the tail of one of these drops, known as *Rupert's drops*, be suddenly nipped off, the glass flies to pieces with a kind of explosion, and is shattered to powder. This effect appears to be due to the unequal tension to which the particles composing the drop are subjected, owing to the sudden cooling of the outer surface of the glass, while the interior is still dilated: as the mass cools, the particles within, by adhesion to the external solid portion, are still kept in their dilated state; but a very slight disturbance of their relative position suffices to overcome their equilibrium, and when once the mass gives way at any one point, the cohesion of the whole is suddenly destroyed.

R. de la Bastie's 'toughened' or 'hardened' glass closely resembles this: the glass is heated almost to the temperature at which it begins to soften, and is then suddenly plunged into a bath of fat or oil, or a mixture of the two, at a temperature of about 300° (572° F.). Special mechanical arrangements have to be made to immerse the articles as completely and quickly as possible, and at the same time to prevent the bath taking fire. Pieper has modified the process so far, that he heats the articles to the proper temperature in a specially constructed furnace, and cools them by the sudden injection of superheated steam. The glass prepared in this way is in a physically different state from ordinary glass, is much harder, and can withstand blows fifty times heavier, or more, than the untoughened glass, but it can no longer be cut by the diamond. When broken, however, it goes into comparatively small fragments, the edges of which are far less sharp than those of ordinary broken glass. It also withstands sudden changes of temperature much better than the same kind of glass unhardened.

(641) **Characters of the Salts of Sodium.**—We have no good direct tests for the salts of this metal, as it forms scarcely any insoluble compounds. Its most insoluble salt is what Fremy has

termed sodic bimetantimoniate (1009), which is deposited in transparent octohedra when a solution of freshly prepared *hydric potassic metantimoniate* is added to a neutral solution containing sodium, provided that the liquid has been previously freed from all bases except the alkalies: 1 part of sodium in 10,000 of water will produce a precipitate with this test after twenty-four hours. In analysis, a salt of sodium is concluded to be present when the absence of every other metal has been proved, and yet a saline residue remains, which, with platinic chloride, gives yellow striated prismatic crystals of the platinochloride, $2NaCl.PtCl_4.6OH_2$, by spontaneous evaporation. Andrews (*Chem. Gaz.*, x. 378) has pointed out a property of this salt which admits of its identification in extremely minute quantities; a drop of the solution suspected to contain sodium is mixed with a minute quantity of a solution of platinic chloride, and allowed to evaporate in a warm place; if, before it is quite dry, it be placed in the field of the microscope, and examined by means of polarized light, minute crystals of the sodic platinic chloride will be distinguished from the other salts with which they are accompanied, by their power of transmitting the polarized light, tinged with various colours, according to the thickness of the crystals. *Before the blowpipe* the salts of sodium are known by the intense yellow which they communicate to the outer flame, if a fragment be introduced at the point of the blue cone upon a loop of platinum wire; the same phenomenon occurs when an ordinary Bunsen burner is employed, and the flame, when examined by the spectroscope, is seen to consist of a pure yellow light exactly coincident in position with the double line D in the solar spectrum, fig. 83, *Na*, Part I.

The salts of sodium are in general more soluble than those of potassium, the sulphates of the two metals affording a striking instance of this difference; many of the sodium salts also effloresce when exposed to the air, whilst those of potassium, on the other hand, frequently déliquesce, a fact well exemplified by the carbonates of the two metals.

§ III. LITHIUM: L=7.

(642) **LITHIUM**: *Density*, 0·5936; *Fusing-pt.* 180° (356° F.).—Lithium, the metallic base of the third of the alkalies, is of comparatively recent discovery, and derives its name from λίθος (a stone), as it was at first found only in the mineral kingdom. It was supposed to be a very rare substance, but Bunsen and Kirchhoff have shown, by the method of spectrum

analysis, that it is widely distributed although generally in minute quantity: they found it in many micas and felspars, in the ash of tobacco of many kinds, and in several mineral springs. The minerals of most frequent occurrence which contain lithium are the three following:

Lepidolite, or lithia mica	$[(LK)F]Al_2O_3.3SiO_2$?
Triphane, or spodumene	$3(LNa)_2O.4Al_2O_3.15SiO_2$
Petalite	$3(LNa)_2O.4Al_2O_3.30SiO_2$.

They yield this alkali in proportion varying from 3 to 6 per cent. of their weight.

Metallic lithium is easily reduced from its fused chloride, or a mixture of the chloride with ammonic chloride, by means of an electric current obtained from six to twelve pairs of the nitric acid battery. The metal is of a white colour, and is fusible at 180° (356° F.). It is harder than potassium, but softer than lead, and admits of being welded by pressure at ordinary temperatures; it can be squeezed into wire, which, however, is inferior in tenacity to lead wire of the same dimensions. Lithium appears to be the lightest solid body known; it floats in naphtha, and has a density of only 0·5936. At high temperatures it is volatile, and it may be distilled at a full red heat in a current of hydrogen. It cannot, however, be obtained by processes similar to those employed for potassium and sodium. A fragment of lithium burns upon a plate of mica with a very brilliant white light, emitting a heat sufficiently intense to melt a hole in the mica; when thrown upon water it swims and becomes oxidized, like sodium. If thrown into sulphuric or nitric acid it usually takes fire. Like potassium and sodium it dissolves in liquefied ammonia forming a blue solution.

(643) **LITHIC CHLORIDE**, or *Chloride of lithium* ($LCl.2OH_2$ =42·5+36), is fusible at a dull red heat: it crystallizes at temperatures above 15° (59° F.) in anhydrous octohedra; but below 10° (50° F.) in square prisms with $2OH_2$: it is one of the most deliquescent salts known. If its aqueous solution be evaporated at a high temperature, it loses a portion of its chlorine, whilst lithia is formed. Lithic chloride is very soluble in alcohol, and in a mixture of equal parts of alcohol and ether; as this mixture does not dissolve the chlorides of sodium and potassium, it may be used to separate chloride of lithium from these salts. The late Professor Miller found this chloride abundantly in a hot saline spring in Clifford United Mines, in Cornwall, where it occurs to the extent of 26 grains in the gallon, accompanied by a very large proportion of the chlorides of sodium and calcium, and a small amount of cæsic chloride; whilst a salt spring in Huel Seaton copper mine, Cornwall, according to Phillips, contains as much as 34 grains per gallon.

(644) **LITHIA**: L_2O=30.—This was discovered by Arfwedson, in 1818, and may be extracted by carefully levigating the minerals that contain it, and igniting the fine powder with twice its weight of quicklime. The mass is treated with hydrochloric acid, then

with sulphuric acid, and the lithic sulphate is dissolved out from the calcic sulphate; the last traces of calcium are removed from the solution of lithic sulphate by ammonic oxalate. This solution may then be deprived of sulphuric acid and converted into caustic lithia, by the addition of baryta water; the solution on evaporation in vacuo yields lithic hydrate, $LHO.OH_2$, which is slightly hygroscopic.

Troost (*Ann. Chim. Phys.*, 1857, [3], li. 103) considers it to be more advantageous to melt 10 parts of the powdered lepidolite with 10 of baric carbonate, 5 of baric sulphate, and 3 of potassic sulphate. The fused mass separates into two portions, a heavy transparent glass, and a supernatant white slag; this white mass consists of a mixture of the sulphates of barium, potassium, and lithium, and contains nearly all the lithium. The sulphates of the alkali-metals are separated from that of barium by washing, and a portion of the potassic sulphate is removed by crystallization. The remaining potassic and lithic sulphates may be converted into chlorides by the addition of baric chloride, and the two chlorides separated by evaporating to dryness and digesting them in a mixture of equal parts of alcohol and ether, which dissolves the lithic chloride only.

In Schering's manufactory, this process has been considerably improved and modified. The finely-ground lepidolite is made into a paste with concentrated sulphuric acid, and after being allowed to stand some time is heated in a reverberatory furnace, and the product completely exhausted with water: the aluminium is then removed by adding the requisite quantity of potassic sulphate and separating the alum as far as possible by crystallization, the remainder of the alumina being precipitated by lime. The sulphates in solution are then converted into chlorides by means of baric chloride, the liquid evaporated to dryness, and the residue treated with absolute alcohol which dissolves lithic and calcic chlorides. From this mixture pure lithic chloride may be obtained by precipitating the calcium with ammonic oxalate, adding a little ammonic sulphide to throw down traces of the heavy metals, evaporating the clear solution, and fusing the residue in a silver vessel.

Lithic Hydrate, LHO, fuses easily below redness, and corrodes platinum vessels powerfully: silver capsules should therefore always be used in preparing it. This action upon platinum is one of the best indications of the presence of lithium. It appears to be due to the formation of an unstable *peroxide of lithium*, which imparts its oxygen rapidly to the platinum.

(645) **LITHIC SULPHATE**, or *Sulphate of lithium*, $L_2SO_4.OH_2 = 110 + 18$; *Density*, 2·02, crystallizes in flat tables, which are very soluble in water. There appears to be no acid sulphate of lithium, although a potassic lithic sulphate may be obtained consisting of $LKSO_4$.

(646) **TRILITHIC PHOSPHATE**, or *Phosphate of lithium*, $L_3PO_4 = 116$, is one of the most characteristic salts of this alkali: it is insoluble in water containing phosphates of the alkalies, and in alkaline solutions, but very soluble in acids even when very

dilute. In order to prepare it, caustic soda is added to the solution of a pure salt of lithium until it has an alkaline reaction, hydric disodic phosphate is then added, the liquid is boiled, and left to stand for at least 12 hours. A heavy granular crystalline deposit of trilithic phosphate gradually forms. This salt fuses with sodic carbonate to a glass which is transparent whilst hot, but becomes opaque on cooling; the transparency of the hot bead furnishes a distinction between trilithic phosphate and the phosphates of the earths, which give an opaque bead both when hot and when cold. The salt supposed by Berzelius to be a sodic lithic phosphate, appears to have been a mixture, and not a definite compound. A monolithic phosphate, LiH_2PO_4, is also known.

(647) **LITHIC CARBONATE,** or *Carbonate of lithium,* $L_2CO_3=74$, is only sparingly soluble in water, but is rather more soluble in a solution of carbonic acid. It may be prepared by decomposing pure lithic chloride with ammonic carbonate and washing the precipitate with 60 per cent. alcohol until free from chlorides: it gives an alkaline reaction with turmeric. At a dull red heat it melts into a white enamel, and by prolonged ignition loses a large portion of its carbonic anhydride.

(648) **Characters of the Salts of Lithium.**—Generally speaking the salts of lithium are remarkably fusible; many of them are very deliquescent. They have a burning saline taste, and are distinguished by yielding, with *potassic carbonate,* a white precipitate of lithic carbonate in cold concentrated solutions, but the precipitate disappears on adding water and applying heat; this reaction is less delicate when salts of ammonium are present. On the addition of *hydric disodic phosphate* to solutions which are neutral or alkaline, trilithic phosphate is formed; it is soluble in the acids and in solutions of salts of ammonium. *Before the blowpipe* the salts of lithium communicate a purplish red colour to the flame, which is masked by the presence of salts of sodium in very small proportion. By means of the spectroscope the occurrence of very minute traces of lithium may be discovered by a brilliant crimson band, which has a refrangibility between that of the lines B and C of the solar spectrum. At very high temperatures a faint band in the orange may sometimes be seen. In these two lines the whole light of the lithium spectrum is contained when produced by the flame of a Bunsen gas-burner (Part I. fig. 83, *Li*). When lithium salts are heated on platinum foil they corrode it rapidly.

§ IV. RUBIDIUM: Rb=85·47.

(649) **RUBIDIUM**; *Density*, 1·52; *Fusing-pt.* 38°·5 (101°·3 F.).—Rubidium derives its name from *rubidus* (dark red), because the spectrum of the light produced when its salts are volatilized in the flame of a Bunsen gas-burner, exhibit a remarkable pair of red lines, less refrangible than Fraunhofer's line A (Part I. fig. 83, *Rb*). Rubidium was discovered in 1860 by Bunsen and Kirchhoff during their investigations on the spectra of artificial flames (*Ann. Chem. Pharm.*, 1861, cxix, 107, and 1862, cxxii. 347). It is usually present in small quantity in lepidolite, and traces of it occur in many of the mineral springs of Germany. It has also been found by Grandeau (*Ann. Chim. Phys.*, 1863, [3], lxvii. 155; comp. Pfeiffer, *Ding. Poly. Jour.*, 1872, ccvi. 498) in minute quantity in beet-root, in tobacco, and in the ashes of a great variety of plants, being sparingly, but very widely, distributed. On treating lepidolite with hydrofluoric acid, adding excess of chalk, filtering, precipitating with sodic carbonate and sulphide, a solution is readily obtained containing nothing but salts of the alkali-metals; the separation of rubidium from other metals is founded upon the comparative insolubility of the chloride of rubidium and platinum; the processes will be described when speaking of the extraction of cæsium (656).

Metallic rubidium was extracted by Bunsen from the charred acid tartrate, 70 grams of which when distilled furnished about 5 grams of a brilliant silver-white metallic mass. It tarnishes rapidly on exposure to the air, becoming coated with a blue suboxide; in a few moments it takes fire spontaneously. At −10° (14° F.) it is soft, like wax; at 38°·5 (101°·3 F.) it melts; and at a heat below redness it furnishes a blue vapour with a shade of green. Rubidium is decidedly more electropositive than potassium: when thrown upon water it takes fire and burns with a flame resembling that of potassium.

(650) **RUBIDIC CHLORIDE**, or *Chloride of rubidium*, RbCl=121, crystallizes with difficulty in cubes: it is easily fusible, and is more soluble than potassic chloride, but is permanent in the air. With platinic chloride it forms a sparingly soluble double chloride, $2RbCl.PtCl_4$, which requires 185 times its weight of boiling water for solution. If fused rubidic chloride is submitted to electrolysis, the reduced metal is dissolved by the chloride and forms a smalt-blue subchloride.

(651) **RUBIDIC HYDRATE**, RbHO = 102·5, is a powerful alkaline base which may be obtained from the carbonate or sulphate by processes resembling those adopted for potassic hydrate. It is very deliquescent, is soluble in alcohol, and absorbs carbonic anhydride with avidity.

(652) **RUBIDIC SULPHATE**, Rb_2SO_4 = 266·9, crystallizes in hard, brilliant, anhydrous prisms, isomorphous with those of potassic sulphate, but it

is much more soluble than that salt. A true *rubidium alum* may be obtained in octohedral crystals by allowing a mixture of rubidic and aluminic sulphates to evaporate spontaneously. An *acid sulphate* of rubidium, $RbHSO_4$, is also known.

(653) **RUBIDIC NITRATE**, $RbNO_3 = 147{\cdot}5$, is a very soluble salt requiring 2·3 parts of water at 10° (50° F.) for its solution. It crystallizes in dihexagonal prisms, terminated by dihexagonal pyramids.

(654) **RUBIDIC CARBONATE**, $Rb_2CO_3 = 230{\cdot}9$, is a deliquescent salt which may be obtained with difficulty in crystals with OH_2. It absorbs carbonic anhydride with avidity and furnishes a *hydric rubidic carbonate*, or *bicarbonate*, $RbHCO_3$, which crystallizes in brilliant prisms: they are permanent in the air and insoluble in alcohol. When heated, they are converted into the normal carbonate, which by further elevation of temperature fuses easily.

(655) **Characters of the Rubidium Salts.**—The salts of rubidium are with difficulty distinguished from those of potassium. The rubidic platinic chloride is the most characteristic: by its sparing solubility in boiling water, it may be separated from the potassium salt, which is soluble in one-eighth of the quantity of water required for solution of an equal weight of the rubidium salt. The most certain test is the appearance of the flame in the spectroscope, which exhibits two characteristic lines in the red, less refrangible than that of potassium, and two lines in the blue, intermediate between those of cæsium and potassium.

§ V. CÆSIUM: Cs = 132·56.

(656) This metal derives its name from *cæsius*, sky-blue, in allusion to the two brilliant blue bands produced by it in the spectrum of a gas-flame in which its compounds are undergoing volatilization. It was discovered by Bunsen and Kirchhoff at the same time as rubidium (*Pog. Ann.*, cxiii. 1861, 377), which indeed it usually accompanies in very small quantity. Cæsium was originally discovered amongst the saline constituents of the Dürkheim spring, the water of which contains about one five-millionth of its weight of a salt of cæsium, or about 1 grain in 140 gallons. The spring in Wheal Clifford, Cornwall, contains about 1·71 parts of cæsic chloride in one million, or 1 grain in 12 gallons (*Col. P. Yorke*). Ordinary lepidolite contains only traces; but a variety of this mineral from Hebron, in the State of Maine, N.A., was found, by Johnson and Allen, to yield 0·24 per cent. of the metal. Still more recently, Pisani has found cæsium to the extent of 34 per cent. in a rare mineral named pollux, analogous to analcime, obtained from the island of Elba (*Compt. Rend.*, 1864, lviii. 714).

Böttger, in examining the salt obtained by evaporating down the mother-liquor of the Nauheim spring, discovered in it

cæsium, rubidium, and thallium. He, indeed, recommends it as the cheapest source of the two new alkali-metals; they exist in the spring in the form of chlorides.

In order to obtain the compounds of cæsium, advantage is taken of the insolubility of the cæsic platinic chloride, which is but little more than half as soluble in boiling water as the corresponding salt of rubidium. The mixture which contains the rubidium and cæsium is freed from compounds of the earths and other metals by the ordinary methods, and the residue, which contains salts of the alkalies only, is mixed with a solution of platinic chloride, which if added in excess precipitates nearly the whole of the rubidium and cæsium, together with a large proportion of potassium. By continued boilings of the precipitate with small quantities of water, repeated eighteen or twenty times in succession, so long as the washings have a yellow colour, the potassium salt is removed. The platinum salt is reduced by heating it in a current of hydrogen. The mixed rubidic and cæsic chlorides are dissolved out by water, and converted into sulphates by heating them with an excess of sulphuric acid, which is expelled by ignition. On adding pure baryta water to the solution of the sulphates, the alkalies are obtained in the caustic state, and may then easily be converted into carbonates, either by carbonic acid or ammonic carbonate. Once more the solution of the mixed carbonates is evaporated to complete dryness, and treated with boiling absolute alcohol, which dissolves out cæsic carbonate, and leaves the rubidic carbonate. On evaporation of the alcoholic solution a tolerably pure cæsic carbonate is obtained.

The best plan of separating cæsium from rubidium, according to Allen and Johnson, consists in taking advantage of the inferior solubility of the hydric rubidic tartrate, $RbHC_4H_4O_6$. The mixed carbonates are to be neutralized with tartaric acid, and then a quantity of the acid is added sufficient to convert the rubidium into the acid tartrate, leaving the cæsium in the solution as normal tartrate, which is deliquescent. The solution is concentrated by evaporation until it is nearly saturated at the boiling-point. The rubidium salt crystallizes out on cooling, and may be purified by recrystallization. This acid tartrate, $RbHC_4H_4O_6$, requires 8·5 parts of boiling and 94 parts of water at 25° (77° F.) for solution The acid cæsium salt is soluble in its own weight of boiling water, and in 10 parts of water at 25° (77° F.); the normal salt is deliquescent (Bunsen, *Pog. Ann.*, 1863, cxix. 1).

An amalgam of cæsium may be obtained by submitting a solution of the chloride to electrolysis, employing a globule of mercury for the negative electrode. This amalgam is even more electropositive than that of rubidium, so that cæsium is the most electropositive element as yet discovered.

(657) **CÆSIC CHLORIDE**, $CsCl = 168{\cdot}1$, crystallizes in cubes, and is not deliquescent when pure: it melts at a low red heat. 100

parts of cæsic chloride contain 21·07 parts of chlorine, whilst an equal weight of rubidic chloride contains 29·7, and of potassic chloride 47·5 of chlorine.

(658) **CÆSIC PLATINIC CHLORIDE,** $2CsCl.PtCl_4 = 675·2$, crystallizes in yellow transparent octohedra: 100 parts of boiling water dissolve 0·377 of the salt (Bunsen).

(659) **CÆSIC OXIDE,** or *Cæsia;* Cs_2O.—Cæsium appears to form two oxides: a blue suboxide, and a powerfully basic oxide corresponding to potash and soda, termed *cæsia*. *Cæsic hydrate,* $CsHO = 149·5$, is very deliquescent, and powerfully caustic: it is readily soluble in alcohol. When heated, it fuses readily, and attacks platinum.

(660) **CÆSIC SULPHATE,** $Cs_2SO_4 = 361·1$, is anhydrous, permanent in the air, but very soluble in water. It forms double salts with magnesic sulphate, and other sulphates of that class, of the form $MgSO_4.Cs_2SO_4.6OH_2$. It also yields a crystallizable alum. A *hydric cæsic,* or *acid sulphate,* $CsHSO_4$, may be obtained in short rhombic prisms.

(661) **CÆSIC NITRATE,** $CsNO_3 = 194·6$, is anhydrous, and isomorphous with rubidic and potassic nitrates. It is permanent in the air, has a cooling taste, and is soluble in ten times its weight of cold water.

(662) **CÆSIC CARBONATE,** or *Carbonate of cæsium,* $Cs_2CO_3 = 325·1$, is deliquescent; it requires five times its weight of boiling alcohol for solution. *Hydric cæsic carbonate,* or *acid carbonate,* $CsHCO_3 = 193·6$, may be obtained in brilliant prismatic crystals, which are permanent in the air.

(662*a*) **Characters of the Cæsium Salts.**—The salts of cæsium are not easily distinguished from those of potassium and rubidium, except by the characteristic lines in the spectrum of their flame (Part I. fig. 83, *Cs*). When, however, a solution of antimony chloride in concentrated hydrochloric acid is added to a solution of a cæsic salt, a crystalline precipitate consisting of a double *chloride of antimony and cæsium,* $SbCl_3.6CsCl$, is produced (Godeffroy, *Deut. chem. Ges. Ber.*, 1874, vii. 375; and 1875, viii. 9). It is sparingly soluble in dilute boiling hydrochloric acid, but almost insoluble in the cold: water decomposes this compound. The corresponding rubidium compound is readily soluble in strong hydrochloric acid. Cæsium differs from rubidium also in yielding a very difficultly soluble silicotungstate, which falls as a white crystalline precipitate on adding cæsic chloride to a solution of silicotungstic acid. It requires 20,000 parts of cold water for solution, whilst the corresponding rubidium compound only requires about 150. Both the compounds, however, are insoluble in dilute hydrochloric acid and in water.

§ VI. AMMONIUM: $NH_4 = 18$ (*hypothetical*).

(663) **Action of Oxyacid Anhydrides on Ammonia.**—When dry gaseous ammonia, NH_3, is presented to the anhydrides of the oxyacids, such as sulphuric, SO_3, sulphurous, SO_2, or carbonic, CO_2, the gas enters into combination with the anhydride, and a peculiar compound is formed, in which Laurent and Gerhardt maintained that only one-half of the ammonia exists in the form of an ordinary ammoniacal salt, the other half having entered into combination with the elements of the anhydride, to form a compound termed an amidated acid; the product obtained differs, therefore, in many important particulars from the compound which would be obtained by neutralizing with ammonia a solution of the same acid in water. In the latter case one of the ordinary 'salts of ammonia,' as they were formerly termed, is produced; in the former case an ammoniacal salt of a new amidated acid would be the result.*

The general properties of these bodies may be illustrated by examining the several combinations formed by sulphuric and sulphurous anhydrides with dry ammoniacal gas.

(664) **Sulphuric Ammonide, Sulphat-ammon, Ammonic Sulphamate,** $(NH_3)_2SO_3$, or $[NH_2(SO_2)''(ONH_4)]$.—Two distinct compounds may be obtained by the action of dry ammonia on sulphuric anhydride. When a current of dry ammoniacal gas is passed over sulphuric anhydride, placed in a flask, and maintained at a low temperature, a hard gummy mass is produced, which when exposed to the air absorbs moisture and gradually deliquesces. The liquid thus obtained is saturated with baric carbonate, in order to remove the excess of acid, and is then evaporated; it yields large transparent crystals derived from an octohedron with a square base. This compound, the *parasulphat-ammon* of Rose, is identical with the *sulphamide*, $(NH_3)_2SO_3$, of Jacquelin, prepared by passing the vapour of sulphuric anhydride into ammoniacal gas in excess, fusing the solid compound in an atmosphere of ammonia, and crystallizing the product from water. Berghund (*Deut. chem. Ges. Ber.*, 1876, ix. 253) has found that the

* These compounds of ammonia with the anhydrides are often incorrectly spoken of as *amides*. The amides of monobasic acids are, properly speaking, salts of ammonium which have been deprived of 1 molecule of water. Ammonic benzoate, $NH_4C_7H_5O_2$, for example, when deprived of OH_2, furnishes a white fusible volatile solid known as *benzamide*, $NH_2C_7H_5O$. The amides of the dibasic acids are ammonium salts which have been deprived of 2 molecules of water. *Sulphamide* would be $(NH_2)_2SO_2$, and would contain one molecule of water less than sulphuric ammonide. The *ammonides*, or *ammons*, as these compounds of ammonia with the anhydrides of dibasic acids have been termed, contain only one molecule of water less than the ordinary ammonium salts. Ammonic sulphate, for instance, may be represented as $(NH_4)_2SO_4$, whilst sulphuric ammonide contains $(NH_3)_2SO_3$, or $NH_4.SNH_2O_3$. The different compounds obtained from the salts of ammonia by dehydration will be considered amongst the products of organic chemistry.

action of ammonia on chlorosulphuric acid, $SO_2(OH)Cl$, gives rise to a compound identical with this, but which he regards as the diammonic salt of *imidosulphonic acid*, $HO.SO_2.NH.SO_2.HO$, and assigns to it the formula:

$$NH_4O.SO_2.NH.SO_2.NH_4O = (NH_3)_2 2SO_3.$$

It is freely soluble in water, but insoluble in alcohol. Its solution has a bitter taste and acid reaction, but gives no precipitate with barium salts, and none with platinic chloride. When its solution is mixed with one containing an equivalent quantity of baric hydrate, ammonia is evolved, and the filtered liquid on evaporation yields crystals of baric imidosulphonate. Potassic imidosulphonate is also crystalline. By long boiling with water, or with a solution of tartaric acid, the ammonic salt is slowly changed into ordinary ammonic sulphate, and if heated with a free alkali, sulphate of the alkali-metal is speedily produced, and ammonia is expelled.

If ammoniacal gas in excess be made to act upon sulphuric anhydride, another compound, the *sulphat-ammon* of Rose, or *ammonic sulphamate*, $(NH_3)_2SO_3$, of Woronin, is obtained. It does not crystallize. Berghund assigns to it the formula $NH_4O.SO_2.N(NH_4).SO_2.NH_4O$, and regards it as a basic derivative of imidosulphonic acid, this acid being capable of forming two series of salts; neutral of the general formula, $M_2O_2(SO_2)_2NH$, and basic, of the formula $M_2O_2(SO_2)_2NM$.

(665) **Sulphamic Acid.**—The true *sulphamic acid*, or *amidosulphonic acid*, $HO.SO_2NH_2$, is formed on boiling a neutral salt of imidosulphonic acid, the reaction in the case of the baric compound being:

$$2BaO_2(SO_2)_2NH + 2OH_2 = Ba(O.SO_2NH_2)_2 + BaSO_4 + H_2SO_4.$$

By long-continued boiling the baric sulphamate undergoes decomposition, forming baric and ammonic sulphates, $Ba(O.SO_2NH_2)_2 + 2OH_2 = BaSO_4 + (NH_4)_2SO_4$. In preparing the baric salt of this acid, an aqueous solution of ammonic or baric imidosulphonate is boiled until it acquires a strongly acid reaction. It is then supersaturated with baryta water, boiled until ammonia ceases to be given off, and the excess of baryta precipitated by carbonic anhydride. On filtering and evaporating, *baric sulphamate* is obtained in long silky needles (Berghund, *ibid.*, 1876, ix. 1896).

(666) **Sulphit-Ammon, or Sulphurous Ammonide,** $(NH_3)_2SO_2$ $[NH_2(SO)''(ONH_4)]$.—If dry gaseous sulphurous anhydride be mixed with an excess of perfectly dry ammoniacal gas, 1 volume of the anhydride and 2 of ammonia combine and form a yellow, amorphous, volatile, deliquescent compound, which undergoes gradual decomposition when dissolved in water (Rose).

If the sulphurous anhydride be in excess, a different compound is formed, NH_3SO_2, corresponding in composition to hydric ammonic sulphite from which 1 molecule of water has been abstracted: $NH_3SO_2 = NH_4HSO_3 - OH_2$. It is a reddish-yellow, crystalline, volatile substance, freely soluble in water: when in solution, it is speedily decomposed into ammonic sulphate and trithionate; $4(NH_3SO_2) + 2OH_2 = (NH_4)_2SO_4 + (NH_4)_2S_3O_6$. No such decomposition occurs when the ordinary hydric ammonic sulphite is dissolved in water.

Phosphoric and carbonic anhydrides also form ammonides, which are analogous to those just described.

(667) **Action of Anhydrous Hydracids on Ammonia.**—Dry ammoniacal gas likewise unites with facility with the anhydrous hydracids; the compounds which are thus produced do not correspond in properties to the ammonides, but, on the contrary, form ordinary ammonium salts. For example, dry hydrochloric acid and dry ammoniacal gases unite with the greatest readiness, and a white solid compound is produced, which is ordinary 'sal ammoniac,' or ammonic chloride; when dissolved in water it gives with solution of argentic nitrate the usual curdy precipitate indicative of chlorine, and with platinic chloride the usual yellow double salt characteristic of ammonium salts is deposited.

(668) **THEORY OF AMMONIUM.**—The difference between the characters of the compounds which dry ammonia forms with the oxyacid anhydrides, and those which it produces with the anhydrous hydracids was explained by Berzelius with the aid of a hypothesis originally suggested by Ampère, which has been termed 'the ammonium theory,' by the adoption of which the salts of ammonia admit of being considered as possessing a constitution analogous to that of the metallic salts.

According to this view, the compounds which are frequently spoken of as salts of ammonia with the oxyacids do not contain ammonia at all, but a compound in which the elements of a molecule of water having been added to those of two of ammonia [$2NH_3+OH_2$]; in consequence of the assimilation of this molecule of water, the substance which is formed may be regarded as $(NH_4)_2O$, ammonic oxide, analogous to potassic oxide, K_2O, and the basyl of the salts which it yields would be the compound body ammonium, NH_4, which takes the place of a metal. Anhydrous ammonia, when it unites with the oxyacid anhydrides, must therefore produce bodies very different from those obtained by the combination of hydrated ammonia with the anhydrides, or by the combination of ammonia with the acids, as may be seen, for instance, by comparing the formula of the compound of ammonia with sulphuric anhydride, and with sulphuric acid:

$$\underset{\text{Sulphuric ammonide.}}{(NH_3)_2SO_3} \quad ; \quad \underset{\text{Ammonic sulphate.}}{(NH_4)_2SO_4}.$$

It is likewise easy to see why, by the combination of anhydrous ammonia with a hydracid equally free from water, a true ammonic salt should be formed: for instance, hydrochloric acid and ammonia by their union yield ammonic chloride, a salt which obviously presents the closest analogy with the metallic chlorides; $NH_3+HCl=(NH_4)Cl$.

With the oxyacids, then, on the one hand, and with their

anhydrides on the other, ammonia forms two distinct classes of compounds; the more important class constitutes the normal salts of the alkali in which the elements of water are necessarily present; the other class consists of the ammonides already described.

The theory of ammonium is supposed to derive considerable support from the following remarkable experiment:—If an amalgam of potassium or of sodium be moistened with a concentrated solution of sal ammoniac, NH_4Cl, the amalgam immediately begins to increase in bulk, and ultimately swells up until it acquires 8 or 10 times its original volume; at the same time it assumes a pasty consistence, but still preserves its metallic lustre. It is generally supposed that this remarkable amalgam consists of a combination of NH_4 (or ammonium) with mercury. The proportion of ammonium present in the amalgam, notwithstanding the great change in bulk and in properties experienced by the mercury, is extremely minute, amounting, according to Gay-Lussac and Thénard, to little more than one two-thousandth of the weight of the mercury. It has been thought that this amalgam is really a kind of froth of mercury, the gaseous portion being hydrogen and ammonia; the amalgam is easily compressed, and when introduced into a syringe, its bulk may readily be reduced by pressure until it is but little more than that of the mercury originally employed; on removing the pressure it again expands (Seely, *Chem. News*, 1871, 169). The amalgam is, however, capable of existing for a short time in vacuo, which it would scarcely do if it were merely a froth of mercury.

(669) **AMMONIC CHLORIDE**, or *Chloride of ammonium*; $NH_4Cl = 53{\cdot}5$; *Density of Solid*, 1·578; *of Vapour, Theoretic*, 0·925; *Observed*, 1·01; *Mol. Vol. of Vapour*, [ ]; * *Rel. wt.* 13·375; *Comp. in* 100 *parts*, HCl, 68·22; NH_3, 31·78.—*Muriate of Ammonia*, or *Sal Ammoniac*, as it is commonly termed, is the most important of the salts of ammonium. It may be formed directly by the union of hydrochloric acid and ammoniacal gases: it was formerly imported from Egypt in considerable quantity as a product of the distillation of dried camel's dung, but in this country it is now prepared almost entirely from *ammoniacal liquor*, a waste product from the coal-gas works. Coal contains

* The vapour-volume of this and of several ammonium salts, including the bromide and cyanide, is anomalous, being double that of most compounds. Many chemists consider that in the act of evaporation these compounds are separated into the free hydracid and free ammonia (Part I. *note*, p. 112).

a portion of nitrogen, which, during the process of distillation, is partially converted into ammonia; this combines with carbonic acid and with sulphuretted hydrogen: these compounds are condensed with the gas liquor, from which the ammonia is subsequently extracted. The best process for preparing sal ammoniac consists in neutralizing the gas liquor with hydrochloric acid. For this purpose the liquid is pumped up from a tank into the decomposer—a large wooden vat closely fitted with a cover, connected with flues for carrying off the gaseous products: the acid in suitable quantity is placed in jars, from which it is drawn off slowly by siphons, and is thus allowed to mix gradually with the liquor, abundance of gas is disengaged, and is made to pass through a fire, where the sulphuretted hydrogen is burned; much of the tarry matter (derived from the coal) which was held in solution, is deposited during this operation, and the liquid froths up considerably, any loss which might be thus occasioned being prevented by the use of a waste-pipe, by which the overflow is carried back into the tank below. When the liquor has thus been neutralized, it is run into a covered evaporating pan, where the remaining portions of sulphuretted hydrogen are expelled; after further concentration it is drawn off into shallow wooden vessels, lined with lead, to crystallize: the crystals thus obtained are drained, and the mother-liquor is again concentrated. The rough crystals are next heated in a cast-iron pan, to a point approaching that at which sublimation commences; a good deal of tarry matter, which the salt still retains, is expelled during this roasting. The salt is then sublimed in a strong cylindrical iron pot, furnished with a leaden or iron cover lined with fire-clay; the fire underneath is gradually raised, and the salt sublimes and is deposited in a large dome-shaped cake on the inner surface of the cover.

The liquors which are condensed during the distillation of bones in closed iron cylinders, in the process of preparing animal charcoal, are highly charged with an impure ammonic carbonate contaminated with volatile oily and tarry products derived from the action of heat upon animal matter; these liquors furnish a source of ammoniacal salts of some importance: formerly this liquid, after being subjected to a partial purification, was commonly known as *spirit of hart's-horn*, because a similar liquor was originally obtained by the distillation of horn shavings.

Sublimed ammonic chloride forms semi-transparent, tough, fibrous masses. It is very soluble in water, 100 parts of which at 15° (59° F.) dissolve 36 parts, and at the boiling-point, 88·9

parts of the salt: a great reduction of temperature occurs while it is undergoing solution, and it is hence employed as a common ingredient in freezing mixtures; it crystallizes usually in an arborescent form, but sometimes in cubes and octohedra. Sal ammoniac has a sharp, acrid taste; it is slightly soluble in alcohol. When heated, it sublimes below redness, without previously undergoing fusion. It has a strong tendency to form double salts with the chlorides more electronegative than itself. The compounds of many metals which form volatile chlorides, such as the arseniates and arsenites, the antimoniates and the stannates, when heated with ammonic chloride, lose the arsenic, antimony, and tin in the form of chlorides of these metals; and the salts of lead, iron, zinc, and aluminium are decomposed and completely volatilized when ignited with a large excess of sal ammoniac. Rose observed that all the basic protoxides of the form M″O, such as protoxides of iron, cobalt, and manganese—and oxides of the form M_2O, such as suboxide of copper, also decompose ammonic chloride when heated with its solution, the ammonia being displaced by the metallic oxide, and a fixed metallic chloride being formed, whilst not one of the sesquioxides has this power.

(670) **AMMONIC IODIDE**; NH_4I.—This is a salt which crystallizes in cubes: it is used to some extent by the photographer, and may be obtained by decomposing calcic iodide by the addition of a mixture of ammonia and ammonic sesquicarbonate in slight excess; the solution filtered from the precipitated calcic carbonate yields pure ammonic iodide.

(671) **Solution of Ammonia.**—The preparation of ammoniacal gas and of its aqueous solution have been already described (391, 392). The solution in water has an intensely alkaline reaction, and may be regarded as a solution of ammonic hydrate, $NH_4.HO$; but when heated, pure gaseous ammonia, NH_3, alone is expelled, and by passing the gas through a tube filled with quicklime, to absorb the water which it carries over with it, ammonia may be obtained in a state of purity. The solution in water, when neutralized by acids and evaporated, yields the ordinary ammonic salts.

The compounds of ammonium are continually receiving fresh applications. The sulphite and the chloride are used in the preparation of ammonium-alum, as a substitute for the corresponding potassium compound; for agricultural purposes the sulphate is largely used as a manure for cereal crops. Caustic ammonia is employed by the dyer as a solvent for cochineal; it is essential in the preparation of orchil and the lichen colours. A remarkable application of ammonia has also lately been made

in Carré's refrigerating machines (*note*, Part I. p. 387), which are extensively used in chemical operations on a large scale.

(672) **SULPHIDES OF AMMONIUM.**—Ammonium forms several sulphides which are freely soluble in water. *Diammonic sulphide*, or the *protosulphide*, $(NH_4)_2S$, may be obtained in colourless crystals by distilling a mixture of potassic sulphide and ammonic chloride; collecting the product in a receiver, cooled to $-18°$ ($0°{\cdot}4$ F.). At the ordinary temperature it gives off ammonia, and leaves ammonic hydric sulphide: its solution may be prepared by dividing a solution of ammonia into two equal portions, through one of which sulphuretted hydrogen is passed as long as it is absorbed; the saturated liquid is then added to the second portion of the solution. It is, however, possible, although not probable, that the two solutions, $NH_4.HS$ and $NH_4.HO$, may remain mixed instead of decomposing each other to form $(NH_4)_2S+OH_2$. This liquid dissolves many of the sulphides of the metals which furnish acids with oxygen, and forms double sulphides with them (568, 578). Many of these double sulphides may be obtained in crystals; this, for example, is the case with those which contain the diantimonic and diarsenic pentasulphide, and the molybdic trisulphide.

Diammonic disulphide, $(NH_4)_2S_2$, may be obtained in large yellow, transparent, very deliquescent crystals, by passing sulphur vapour and dry ammonia through a red-hot porcelain tube. In the hydrated form it has been long known as *Boyle's fuming liquor*, and is prepared by calcining 3 parts of slaked lime with 2 of sulphur, and distilling 3 parts of this mixture with 2 of sal ammoniac and 1 part of sulphur: a yellow, oily, fœtid liquor, which fumes in the air, passes over, and on cooling it deposits deliquescent yellow lamellar crystals; acids disengage hydrosulphuric acid from it, and cause a deposit of sulphur. Its aqueous solution dissolves a large quantity of sulphur, forming a *pentasulphide*, $(NH_4)_2S_5$, which crystallizes from its solution in long orange-yellow oblique rhombic prisms. Fritsche has also obtained a compound containing $(NH_4)_2S_7$ in ruby red crystals.

(673) **AMMONIC HYDRIC SULPHIDE**, *Sulphhydrate of ammonium*, or *Ammonic thiohydrate*, $NH_4.HS=51$, is the liquid commonly used as a reagent under the name of hydrosulphate of ammonia: it is formed by saturating a solution of ammonia with sulphuretted hydrogen. This liquid, when newly prepared, is colourless, but it absorbs oxygen rapidly from the air, and becomes yellow from formation of ammonic disulphide, whilst ammonic thiosulphate (hyposulphite) is produced in the liquid; $8NH_4.HS+5O_2=2(NH_4)_2S_2+2(NH_4)_2S_2O_3+4OH_2$. A solution of ammonic hydric sulphide dissolves the sulphides of the electronegative metals as readily as diammonic sulphide does, but sulphuretted hydrogen is liberated: for example, $6NH_4.HS+$

$As_2S_5 = 2(NH_4)_3AsS_4 + 3SH_2$. Ammonic hydric sulphide may be obtained in the anhydrous form, by mixing dry sulphuretted hydrogen with dry ammoniacal gas; 2 volumes of ammonia combine with two of sulphuretted hydrogen, and condense in colourless, transparent, brilliant plates, which are very volatile, and sublime without decomposition; they are very soluble in water.

(674) **AMMONIC SULPHATE**, or *Sulphate of ammonium*, $(NH_4)_2SO_4 = 132$; *Density*, 1·695.—This is prepared in large quantity by subjecting gas liquor to distillation, and condensing the volatilized ammonia in sulphuric acid. The salt crystallizes out from the strongly acid liquor, which is employed to condense fresh ammonia in subsequent operations. On a small scale it may be obtained in a pure form by adding ammonic sesquicarbonate to dilute sulphuric acid so long as any effervescence ensues. It crystallizes in flattened prisms, which are isomorphous with those of potassic sulphate: it is soluble in twice its weight of cold water, and has a sharp disagreeable taste; when heated it decrepitates; at 140° (284° F.) it melts, and between 260° and 315° (500° and 599° F.) it undergoes partial decomposition, ammonic sulphite being among the products. It forms a great number of double salts isomorphous with the corresponding potassium salts. Ammonic sulphate has lately been applied to muslins and other fabrics for the purpose of preventing them from burning with flame in case they should accidentally take fire. The finished goods are dipped into a solution containing 10 per cent. of the salt, and dried in a centrifugal machine, or *hydro-extractor*.

A *hydric ammonic sulphate*, or *acid sulphate* may be formed having the formula $(NH_4)_3H2SO_4$; and a *sodic ammonic sulphate*, $NH_4NaSO_4.2OH_2$, may be readily formed by mixing solutions of sodic and ammonic sulphates in equivalent proportions, and evaporating the liquid until it begins to crystallize.

(675) **AMMONIC NITRATE**, or *Nitrate of ammonium*; $NH_4.NO_3 = 80$; *Density*, 1·635.—This is a salt of some importance to the chemist, as it furnishes him with a ready source of pure nitrous oxide. It is prepared by neutralizing nitric acid with a solution of ammonic sesquicarbonate, and on evaporating the solution the salt crystallizes in long striated anhydrous prisms; by rapid evaporation it is obtained either in a fibrous or in an amorphous mass. It has a bitter acrid taste, is somewhat deliquescent, and during the act of solution causes a great depression of temperature, hence it is often used in frigorific mixtures: when heated to 107°·8 (226° F.) it melts, and at 250° (482° F.) it undergoes complete decomposition, being con-

verted into nitrous oxide and water, in the manner already described (403); $NH_4.NO_3=N_2O+2OH_2$. If thrown on a red-hot plate it melts, hisses, and is dispersed with a faint bluish flame. Dry ammonic nitrate possesses the property of absorbing a large quantity of gaseous ammonia, at the same time becoming liquid. In this way under the ordinary pressure it absorbs one-fourth its weight at 23° (73°·4 F.), and half its weight at 0° (32° F.). This curious substance, which must be regarded as a solution of ammonic nitrate in liquefied ammonia, is a good electrolyte, yielding hydrogen and ammonia at the negative electrode and nitrogen and ammonic nitrate at the positive.

(676) **AMMONIC NITRITE**, $NH_4.NO_2=64$.—This salt may be prepared by decomposing baric nitrite with ammonic sulphate in equivalent proportions, and evaporating the clear solution in vacuo over quicklime, but as it decomposes with great readiness, especially when in solution, much of it is lost. In the dry state it forms a tough, white, crystalline substance, which can be moulded between the fingers. It explodes at about 60°—70° (140°—158° F.), and detonates when struck. The aqueous solution decomposes very quickly, effervescence taking place when it is shaken, from the nitrogen evolved. Ammonic nitrite is formed by the action of hydric peroxide on ammonia, and in small quantity also, according to Weith and Weber (*Chem. Centr.* 1875, 66), when ammonia and nitric oxide are passed into a well-cooled flask.

(677) **CARBONATES OF AMMONIUM.**—Normal ammonic carbonate, $(NH_4)_2CO_3$, is not known in the anhydrous form, although it may be obtained crystallized in elongated plates of the formula $(NH_4)_2CO_3.OH_2$. When carbonic anhydride and dry ammonia are mixed, no matter in what proportions, 2 volumes of ammonia and 1 of carbonic anhydride unite, and are condensed into a white solid; ammonic carbamate being formed: the same reaction occurs when dry ammonia and dry carbonic anhydride are passed into cold absolute alcohol: according to Gerhardt, $2NH_3+CO_2=NH_4.CO_2NH_2$: $[NH_2(CO)''(ONH_4)]$. This compound is rapidly converted by water into normal ammonic carbonate: $NH_4.CO_2NH_2+OH_2=(NH_4)_2CO_3$. There are, however, several compounds of ammonium with carbonic acid.

The most important of these is the mixture of sesquicarbonate and carbamate of ammonium, the so-called *sesquicarbonate*, or *smelling-salts* of the shops, $2(NH_4)_2CO_3.CO_2=236$, or $2(NH_4)_2O.3CO_2$; *Comp. in* 100 *parts*, NH_3, 28·81; CO_2, 55·93; OH_2, 15·26. It is usually obtained as a semi-transparent fibrous

mass, by mixing chalk with half its weight of sulphate or chloride of ammonium, collecting in leaden vessels the crude product which comes over on applying heat, and resubliming the mixture at a temperature of about 65° (149° F.); the salt is received in leaden hoods, in the interior of which it is deposited. During this process a large quantity of free ammonia escapes, because the normal carbonate cannot exist at that temperature. The decomposition of the ammonic chloride may be represented thus:

$$6NH_4Cl + 3CaCO_3 = 3CaCl_2 + 2(NH_4)_2CO_3.CO_2 + 2NH_3 + OH_2.$$

Ammonic sesquicarbonate has a strong pungent smell, like that of pure ammonia, arising from the continual volatilization of ammonic carbonate at ordinary temperatures:

$$2(NH_4)_2CO_3.CO_2 \text{ becoming } 2NH_4HCO_3 + (NH_3)_2CO_2.$$

Owing to this loss of ammonia the salt speedily becomes coated with a white spongy crust of bicarbonate. If the powdered salt be placed upon a filter, and washed with successive small quantities of cold water, the normal carbonate may be gradually dissolved away, and the salt known as the bicarbonate, which is a more sparingly soluble salt, will be left upon the filter. The sesquicarbonate has an acrid taste, and a strongly alkaline reaction. In its ordinary form the sublimed salt has a composition which is exceptional, since in order to convert it into a normal sesquicarbonate it would require an additional molecule of water, which is never found in the commercial salt; it appears to be a mixture or compound of ammonic hydric carbonate with carbamate, and its aqueous solution, if saturated and exposed to a temperature of 0° (32° F.), deposits large, transparent octohedra with a rhombic base, of the hydrated sesquicarbonate, $(NH_4)_4H_23CO_3.2OH_2$. According to the researches of Rose there are several compounds resulting from the combination of the carbonate with different proportions of bicarbonate of ammonium. An elaborate examination of these salts has been made by Divers (*Jour. Chem. Soc.*, 1870, xxiii. 171).

Hydric Ammonic Carbonate, or *Bicarbonate of Ammonium*: $NH_4.HCO_3 = 79$; *Density*, 1·586.—This is isomorphous with the corresponding potassium salt: it is soluble in about 5·5 parts of water at 15° (59° F.) and 9 at 0° (32° F.), and if the solution be heated, carbonic anhydride escapes; when exposed to the air the dry salt becomes slowly volatilized. It may be obtained in large transparent prismatic crystals, derived from a rhombic octohedron, $4NH_4HCO_3.OH_2$, by pouring boiling water upon the

sesquicarbonate, corking the flask, and allowing it to cool, or by saturating an aqueous solution of ammonia with carbonic anhydride. It is sometimes formed spontaneously during the decomposition of guano, and is then deposited in large regularly formed crystals.

Ammonic carbonate combines with many metallic carbonates, forming double salts.

(678) **PHOSPHATES OF AMMONIUM**, corresponding to those of sodium may be formed; but the only one of any importance is the sodic ammonic hydric phosphate, known as *microcosmic salt*, $Na.NH_4.H.PO_4.4OH_2 = 137 + 72$. It is prepared by mixing a hot solution of 6 parts of hydric disodic phosphate with a solution of 1 part of ammonic chloride in the smallest possible quantity of water; sodic chloride remains in solution, and the phosphate crystallizes in large transparent prisms, which are efflorescent in a dry air. It may be purified by a second crystallization from a small quantity of hot water to which a little free ammonia has been added, to compensate for the loss of ammonia which the salt sustains when heated in solution. By ignition, all the ammonia and water are expelled, sodic metaphosphate remains, and fuses into a colourless glass at a red heat. This salt is sometimes employed as a flux for experiments with the blowpipe, as the glass dissolves many metallic oxides, and forms transparent beads, the colour of which is in many cases characteristic of the metal dissolved.

(679) **Ammoniated Salts.**—Anhydrous ammonia enters into combination with many anhydrous metallic salts in a manner somewhat analogous to that of water of crystallization. In other cases, salts which usually retain water of crystallization lose it either partially or entirely when they combine with ammonia, but the number of molecules of ammonia does not in general correspond to the water of crystallization of the salt. Chloride of silver, of tin, of copper, and of calcium, sulphate of copper, and of zinc, nitrate of silver, and of copper, form compounds of this kind with ammonia. The composition of some of these salts is exhibited in the subjoined table:

			At. wt.	Density.
Ammoniated argentic chloride	...	$AgCl.2NH_3$	177·5	
1. „ cupric „	...	$CuCl_2.6NH_3$	236·4	
2. „ „ „	...	$CuCl_2.4NH_3.OH_2$	220·4	1·671
3. „ „ „	...	$CuCl_2.2NH_3$	168·4	2·194
„ calcic „	...	$CaCl_2.8NH_3$	247	
„ argentic sulphate	...	$Ag_2SO_4.4NH_3$	380	2·918
„ cupric „	...	$CuSO_4.4NH_3.OH_2$	245·4	1·790
„ argentic nitrate	...	$AgNO_3.3NH_3$	221	
„ cupric „	...	$Cu2NO_3.4NH_3$	255·4	1·874

These compounds when exposed to the air lose a portion of their ammonia, and if heat be applied, the ammonia is often entirely expelled, as in the case of ammoniated argentic chloride, the compound originally employed by Faraday for obtaining ammoniacal gas in the liquid form: the argentic chloride is left unaltered when the ammonia is driven off. In other instances the elements of ammonia react upon the salt and decompose it. For example, ammoniated cupric chloride, $CuCl_2.6NH_3$, when heated, first loses 4 molecules of ammonia, and then the residue ($CuCl_2.2NH_3$) undergoes the following decomposition: $6(CuCl_2.2NH_3)=3Cu_2Cl_2+6NH_4Cl+4NH_3+N_2$. The corresponding nickel compound is reduced to the metallic state when heated.

In solution, ammonia also combines with many metallic salts, forming analogous compounds: by exposure to air, the ammonia escapes. Zinc salts form a colourless solution with excess of ammonia; those of cobalt give a brown, which passes into red; whilst both nickel and copper salts give a violet-blue solution.

(680) **Action of Ammonia on Salts in Solution.**—From what has been already stated, it is evident that ammonia does not always act upon metallic salts merely as a powerful base, like potassic or sodic hydrate, the reaction being very often of a more complicated nature. The results produced by the addition of ammonia to a solution of a metallic salt may vary as follows:

1.—If the ammonia be insufficient in quantity to neutralize the whole of the acid contained in the metallic salt, a sparingly soluble basic salt of the metal may be precipitated: in this way basic cupric sulphate, basic plumbic nitrate, or basic aluminic sulphate are formed; for instance, $4CuSO_4+6NH_3+7OH_2=3(NH_4)_2SO_4+CuSO_4.3CuO.4OH_2$.

2.—If the ammonia be present in excess, it may, by reacting upon the acid of the salt, produce with it a soluble ammonium salt, whilst a precipitate of the metallic oxide in a hydrated form is occasioned: as when alumina, chromic oxide, or ferric oxide, is thrown down from its salts: for example,

$$2Fe_23SO_4+12NH_3+9OH_2=6(NH_4)_2SO_4+2Fe_2O_3.3OH_2.$$

3.—Sometimes the ammonia, if in excess, combines with the precipitated oxide, as it does with uranic oxide, when mixed with a solution of uranic nitrate:

$$2(U_2O_2)''2NO_3+6NH_3+3OH_2=4NH_4.NO_3+(NH_4)_2O.2U_2O_3.$$

4.—In other cases a double salt of ammonium and the metal may be precipitated, as when ammonia is mixed with a solution containing phosphoric acid and magnesium, in which case an ammonic magnesic phosphate is formed and deposited in hydrated crystals of the formula $(NH_4)_2Mg_2P_2O_8.12OH_2$: $2MgSO_4 + 2(NH_4)_3PO_4 = 2(NH_4)_2SO_4 + (NH_4)_2Mg_2P_2O_8$.

Reactions corresponding to the four modes of action just indicated frequently occur when a solution of a caustic alkali, such as potassic or sodic hydrate, is mixed with a metallic salt in solution.

5.—A soluble compound may be formed into the composition of which both the metallic oxide and the ammonia enter, and unite with the acid so as to form a species of double basic salt. Magnesic hydrate, hydrated oxide of copper, of zinc, of cobalt, or of nickel, when free from acid, is very sparingly dissolved by a solution of pure caustic ammonia, but a mixture of ammonic chloride, or even of ammonic carbonate with caustic ammonia, dissolves them without difficulty. The compounds thus dissolved are definite in composition, and similar in nature to those enumerated in the table given on page 488 as the result of the action of ammoniacal gas upon the dry salts of the metals. The solutions of these salts in ammonia frequently absorb oxygen rapidly if exposed to the air: salts of iron, manganese, and cobalt furnish examples of this kind.

6.—But it occasionally happens that the elements of ammonia enter into the composition of the salt in a more intimate manner. When a solution of corrosive sublimate, or mercuric chloride, $HgCl_2$, is mixed with a solution of potassic hydrate, a yellow precipitate of mercuric oxide is formed, and potassic chloride remains in solution; $HgCl_2 + 2KHO = HgO + 2KCl + OH_2$; but the case is otherwise if ammonia be used instead of potash; a white precipitate is then formed, the composition of which is unchanged by the addition of an excess of ammonia. Kane (*Phil. Mag.*, 1836, p. 495) showed that this body has a composition which may be represented by the formula of $HgCl_2.N_2HgH_4$. Its formation may be explained by the following equation:

$$2HgCl_2 + 4NH_3 = HgCl_2.N_2HgH_4 + 2NH_4Cl.$$

From this result, conjoined with others obtained from an examination of other ammoniacal derivatives from copper, palladium, and other metals, Kane was led to believe that ammonia was not a direct compound of hydrogen with nitrogen, but rather a combination of an atom of amidogen with one of hydrogen; so

that he represented ammonia as HAd (Ad standing for amidogen, NH_2); the atom of hydrogen being liable to displacement by an equivalent either of mercury or of certain other metals. One molecule of such an amide of mercury ($HgAd_2$) was, according to Kane, contained in white precipitate, in combination with 1 molecule of mercuric chloride.

Later experiments, however, especially those of Hofmann on the formation of bases by substitution from ammonia, have not strengthened the theory proposed by Kane; they have shown that not only does 1 atom of hydrogen admit of being displaced by some equivalent substance, but that each of the 3 atoms of hydrogen in ammonia admits of being thus displaced; nay more, that bodies can be obtained which may be regarded as derived from ammonium, in which all the 4 atoms of hydrogen have been displaced by other equivalent bodies. These investigations point rather to the view that white precipitate is a body corresponding in composition to ammonic chloride, $NH_4.Cl$, but in which 2 atoms of hydrogen are displaced by 1 atom of the dyad metal mercury ($NHg''H_2.Cl$). We shall recur to these investigations when considering the properties of the organic bases.

7.—Within the last few years several remarkable bases which are derived from ammonia have been formed, but into the composition of which certain metals enter. Although these compounds contain the elements of ammonia, and of the oxides of the metals, yet they do not, by means of the ordinary tests, give any indications either of ammonia or of the metals which enter into their composition.

In this manner several series of compounds have been procured, some of which contain platinum, others cobalt, and others palladium; in most instances they form crystallizable and well characterized salts.

Amongst the compounds thus formed, four of those obtained from platinum may be selected by way of illustration. The first of these contains a base for which Gerhardt proposed the name of *platosamine*, N_2PtH_6O; the second, he termed *diplatosamine*, $N_4PtH_{12}O.OH_2$; the third, *platinamine*, $N_2PtH_6O_2.2OH_2$; and the fourth, *diplatinamine*, $N_4PtH_{12}O_2$. The base last mentioned has not as yet been obtained in a separate form.

Each of these bases forms with hydrochloric acid a crystallizable salt, the composition of which is represented by the empirical formula given in the second column of the following table, whilst the third column shows the relation of the compound to the chloride of platinum from which it is obtained; the first two

compounds being derived from platinous chloride, the last two from platinic chloride:

Platosamine dichloride	$N_2PtH_6Cl_2$	or	$PtCl_2.2NH_3$.
Diplatosamine dichloride	$N_4PtH_{12}Cl_2$	„	$PtCl_2.4NH_3$.
Platinamine tetrachloride	$N_2PtH_6Cl_4$	„	$PtCl_4.2NH_3$.
Diplatinamine tetrachloride	$N_4PtH_{12}Cl_4$	„	$PtCl_4.4NH_3$.

(681) **Characters of the Compounds of Ammonium.**—The ammonic salts are colourless; they are all decomposed by heat, unless the acid itself be capable of volatilization, in which case they may generally be sublimed without change. They are distinguished from the salts of all the metals, with the exception of those of the alkaline group, by the absence of any precipitate when their solutions are mixed with a solution of potassic or sodic carbonate. They also appear to undergo dissociation when heated in aqueous solution, for on distilling an aqueous solution of a neutral ammonic salt, the sulphate for example, the distillate will be found to contain free ammonia, whilst the residue in the retort is distinctly acid. It is not improbable, in most cases at least, that the neutral salt becomes decomposed into an acid salt and free ammonia.

The ammonium salts may be recognized by heating them in the solid form with *quicklime* or with *potassic hydrate*, when pungent fumes of ammonia are evolved: if their solutions be boiled with either potassic or calcic hydrate a similar evolution of ammonia ensues, and if the quantity of ammonia be too small to be detected by the smell, a rod dipped into *hydrochloric acid* diluted with an equal bulk of water, produces white fumes when brought into the vapour; these fumes are due to the production of minute particles of sal ammoniac, which are formed by the union of the gaseous ammonia with the vapour of the hydrochloric acid. A characteristic test for free ammonia is the formation of the black iodide of nitrogen in a solution of iodine in potassic iodide; but if the proportion of ammonia be very minute, the only perceptible change is the disappearance of the brown colour of the solution.

Another still more delicate test of the presence of free ammonia is afforded by the use of a liquid consisting of a mixture of equal parts of a saturated solution of arsenious acid and of a solution containing 2 per cent. of argentic nitrate; traces of ammonia cause the formation of the yellow triargentic arsenite (Dr. A. Taylor). This, however, although a sensitive, is not a

characteristic test, since a trace of any free alkali or alkaline earth produces a similar result.

Another very characteristic and extremely delicate method of detecting ammonia and its salts is the Nessler test, which consists of a strongly alkaline solution of mercuric iodide in potassic iodide. It is easily prepared by boiling 35 parts of potassic iodide and 13 of mercuric chloride with 800 of water, until the salts have entirely dissolved. When cold, a saturated aqueous solution of mercuric chloride is cautiously added until the precipitate of mercuric iodide thereby produced is no longer redissolved on agitation. The solution is now rendered alkaline by the addition of 160 parts of potassic hydrate and diluted to 1000. In order to render it sensitive, a small quantity more of the cold saturated solution of mercuric chloride is added, and it is then allowed to settle. If this clear, colourless solution be added in excess to a liquid containing a trace of ammonia, or of any of its salts, it assumes a brown tinge, or furnishes a brown precipitate, according as the proportion of ammonia is less or more; dimercur-ammonium iodide, $NHg_2''I.OH_2$, or ammonium in which 4 atoms of hydrogen are displaced by 2 of mercury, being formed (Nessler). The reaction does not occur in the presence of sulphides or cyanides of the metals of the alkalies. According to Schöyen a still more sensitive reaction, capable of indicating 1 part in 15 millions, may be obtained by adding to about 100 c. c. of water, 1 c. c. of a solution of corrosive sublimate (1 to 30), and the same quantity of a solution of potassic carbonate (1 to 50), the precipitate consisting of $NHg''_2Cl.OH_2$, or the chlorine compound corresponding to Nessler's iodide.

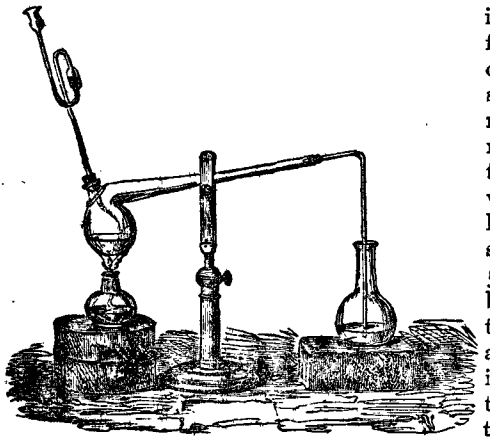
Sodic Phosphomolybdate is also a very delicate test for the presence of an ammonium salt in solution. The mode of preparing and applying it is described under the head of molybdic acid (953).

(682) **Estimation of Ammonia.**—The most accurate method of determining the quantity of ammonia in any substance, if the absence of potassium has been ascertained, consists in precipitating it by *platinic chloride*, observing all the precautions mentioned when speaking of the use of this test for potassium (613); a yellow insoluble double salt falls, consisting of $2NH_4Cl.PtCl_4$; it contains, in 100 parts, 7·62 of ammonia. This salt is easily distinguished from the corresponding potassium compound by heating it to redness, in which case metallic platinum alone

remains; whereas the potassium salt, although decomposed by this treatment, leaves the platinum mixed with potassic chloride, which may be dissolved out of the residue by treatment with water.

(683) **Titration of Ammonia.**—The following method of determining the amount of ammonia in guano or in crude ammoniacal salts will often be found useful. Ten grams of the matter for trial are placed in a small retort, fig. 346, and 100 c. c. of water are added: by means of a bent funnel, 25 c. c. of a solution of potassic hydrate, of density 1·25, is also introduced; 50 or 60 c. c. of liquid is gradually distilled into the flask, which contains 100 c. c. of sulphuric acid diluted to the strength required for the determination of soda for alkalimetrical purposes (610). If the mixture froths up inconveniently when boiled, milk of lime may be substituted for the solution of potash. As soon as 50 or 60 c. c. of liquid has been distilled, the contents of the retort are allowed to cool a little, and 40 c. c. of water is introduced into the retort by the funnel; a second distillation is then proceeded with, until a quantity of water equal to that just added has passed over; 40 c. c. more of water is again added to the contents of the retort, and the distillation is renewed a third time until an equal quantity of water has again passed over. The liquid in the flask is then mixed with a few drops of infusion of litmus, and neutralized, in the usual way, by means of a standard solution of sodic hydrate; the soda solution being of such a strength that one c. c. of it exactly neutralizes an equal measure of the acid liquid originally introduced into the flask. Suppose that this liquid from the flask now requires 67 c. c. of soda solution instead of 100; 33 measures of the acid will have been neutralized by the ammonia; a quantity of ammonia will therefore have passed over equivalent to 3·3 grams of sodic oxide. The corresponding quantity of ammonia may be calculated from the equivalent numbers of the two alkalies:

Fig. 346.



	Eq. Na_2O.		Eq. NH_3.				
Thus,	31	:	17	::	3·3	:	1·809

10 grams of the material operated on in this case would therefore have contained 1·809 grams, or the sample would contain 18·09 per cent. of ammonia.

CHAPTER XVIII.

GROUP II.

METALS OF THE ALKALINE EARTHS.

Metal.	Symbol.	Atomic weight.	Atomic vol.	Density.	Electric conductivity. 68°—62° F.
Barium	Ba	137·0	34·25	4·0	
Strontium	Sr	87·6	34·49	2·54	6·71
Calcium	Ca	40·0	25·35	1·578	22·14

EACH of these metals furnishes two oxides, one of which is basic; the latter combines with water with great energy, forming a hydrate of the formula $M''H_2O_2$. The hydrate absorbs carbonic anhydride rapidly, forming a white carbonate, insoluble in water. The hydrates also absorb chlorine, forming bleaching compounds. Each metal forms several sulphides. The protosulphide is less soluble than the others, and is colourless, whilst all the others are yellow. The sulphates, phosphates, and oxalates are insoluble, or nearly so (see also p. 353).

§ I. BARIUM: $Ba''=137·0$.

(684) **BARIUM** occurs abundantly in the form of sulphate, and is not unfrequently found as carbonate. Davy first obtained it in the metallic state by making mercury the negative electrode of a voltaic battery in a strong solution of baric hydrate; the barium was thus obtained as an amalgam, from which the mercury was expelled by heating it strongly in a green glass tube filled with hydrogen; but it does not appear to have been thus isolated in a state of purity. A crystalline amalgam of barium is also obtained by treating sodium amalgam repeatedly with a hot saturated solution of baric chloride and removing the excess of mercury by pressure in a cloth: when strongly heated in a hard glass tube, together with a little petroleum, to expel the air, the mercury is volatilized, and barium remains in the metallic state. When the metal is procured by the voltaic decomposition of its fused anhydrous chloride, it is of a pale yellow colour; but it is not easily obtained in distinct beads. Barium decomposes water rapidly at ordinary temperatures, and by exposure to the air it is quickly tarnished. It decomposes glass at a red heat.

(685) **BARIC CHLORIDE**, or *Chloride of barium;* $BaCl_2.2OH_2$ $= 208 + 36$; *Density, cryst.* 3·052; *Anhydr.* 3·82; *Comp. in* 100 *parts*, Ba, 65·86; Cl, 34·14.—This salt is obtained by dissolving baric sulphide or carbonate in hydrochloric acid. On the large scale it may be procured by fusing together 1 part of crude calcic chloride (the residue of the preparation of ammonic sesquicarbonate) with 2 parts of powdered native baric sulphate; baric chloride and calcic sulphate are formed; the chloride is washed out rapidly with hot water, and purified by crystallization. Baric chloride crystallizes in flat four-sided tables, containing $2OH_2$, which may be expelled by heat: water dissolves nearly half its weight at 15° (59° F.), and three-fourths at 100° (212° F.): the presence of hydrochloric or of nitric acid greatly diminishes its solubility. A solution of this salt is the usual test for ascertaining the presence of a sulphate in solutions, which it indicates by the formation of a white precipitate insoluble in nitric acid. If anhydrous baryta be introduced into a jar of hydrochloric acid gas it becomes incandescent, baric chloride is formed, and water becomes condensed on the sides of the vessel.

A corresponding *baric bromide*, $BaBr_2.2OH_2$, and *baric iodide*, $BaI_2.2OH_2$, may be obtained; they both crystallize in rhombic prisms, which are very soluble in water.

(686) **BARIC SILICOFLUORIDE**, $BaF_2.SiF_4 = 279$, is formed on adding silicofluoric acid to a solution of a baric salt; it is quickly deposited in microscopic crystals, which are insoluble in an excess of the acid. The salt is anhydrous. It is decomposed by ignition, which converts it into baric fluoride. Strontic silicofluoride is soluble, hence silicofluoric acid may be employed to distinguish salts of barium from those of strontium.

(687) **COMPOUNDS OF BARIUM WITH OXYGEN.**—Barium forms two oxides, a protoxide, baryta, BaO, and a dioxide, BaO_2: the first is the only one which forms salts.

Baric Oxide, or *Baryta;* $BaO = 153·0$; *Density*, 5·456.—On exposing baric nitrate to a red heat in a capacious porcelain crucible, the salt decrepitates, melts, and then boils up and gives off a large quantity of oxygen mixed with nitrogen, leaving baryta as a grey porous mass, which rapidly absorbs moisture and carbonic anhydride if exposed to the air: according to Rammelsberg (*Deut. chem. Ges. Ber.*, 1874, vii. 542), however, it contains more oxygen than that required by the formula BaO, and contains baric peroxide. If mixed with one-eighth of its weight of water it slakes, with great development of heat, and forms a hydrate. Baryta may be fused before the oxyhydrogen blowpipe.

Baric Dioxide, or *Peroxide of barium*, $BaO_2 = 169$, is formed by passing oxygen over anhydrous baryta at a low red heat; or by mixing pure baryta with an equal weight of potassic chlorate and heating to low redness; in the latter case ignition commences at one point, and spreads through the mass like tinder; $3BaO + KClO_3 = KCl + 3BaO_2$: the potassic chloride may be dissolved out by water, and a bulky white insoluble hydrated baric peroxide, $BaO_2.8OH_2$, remains. Brodie, however, finds that it is impossible to convert much more than half the baryta into peroxide by either of these methods. In order to obtain the pure peroxide, he recommends (*Phil. Trans.*, 1863, 409) that the crude material be completely converted into hydrate by pulverizing finely in a mortar, and rubbing it with water. It is then to be mixed gradually with a very dilute solution of hydrochloric acid, taking care that the acid is always in excess. The solution is to be filtered, and baryta water added until the alumina, ferric oxide, and silica are precipitated together with a little baric peroxide, taking care to cool well. The alkaline solution is then to be filtered as rapidly as possible through linen filters, and an excess of baryta water added to the clear filtrate; *hydrated baric dioxide* is thus precipitated in brilliant plates, which are insoluble in water, and may be washed by decantation until free from chlorides: it may be preserved in a moist state in well-closed bottles for any length of time without change, and if pressed between blotting paper it may be rendered anhydrous by desiccation *in vacuo* over sulphuric acid. It is then quite stable, and appears as a fine white powder resembling magnesia (comp. Thomsen, *Deut. chem. Ges. Ber.*, 1874, vii. 73).

By strong ignition baric dioxide again parts with its oxygen. Boussingault (*Ann. Chim. Phys.*, 1852, [3], xxxv. 5) even proposed to make use of caustic baryta as a means of preparing oxygen on a large scale by alternately passing atmospheric air over the baryta raised to a dull red heat, and then expelling the absorbed oxygen by intense ignition; the presence of a small quantity of aqueous vapour greatly assists the expulsion of the oxygen, but the process cannot be worked with facility. When moistened with water the anhydrous peroxide combines with it, and crumbles down to a white powder without evolving any sensible amount of heat; it is used for preparing hydric peroxide (354). Baric peroxide becomes white hot when heated over a spirit-lamp in a rapid current of carbonic oxide or of sulphurous anhydride; small white flames dart out from its surface, whilst baric carbonate or sulphate is formed.

(688) **BARIC HYDRATE**, or *Hydrate of baryta*, BaH_2O_2, may be prepared from baric sulphide by boiling its solution with cupric oxide; baric thiosulphate (hyposulphite) and cuprous sulphide are produced, both of which are insoluble, the baric hydrate remaining in solution: $6BaS + 5OH_2 + 8CuO =$

$5BaH_2O_2 + BaS_2O_3 + 4Cu_2S$: the hot liquid is filtered, and crystals of the pure hydrate, $BaH_2O_2.8OH_2$, of density 1·656, are deposited as the solution cools. The sulphide may also be decomposed by boiling it with zinc oxide instead of cupric oxide. Crystals of baric hydrate may be obtained by adding to a boiling solution of sodic hydrate, of density 1·12, an equivalent quantity of baric nitrate in small quantities at a time. The hot solution is filtered into a vessel covered from the air, and the hydrate is deposited as the liquid cools. The crystals are soluble in 3 times their weight of boiling water, and in 20 of cold water, yielding a strongly alkaline solution. When exposed to the air, both the crystals and the solution absorb carbonic anhydride; the water of crystallization, $8OH_2$, is expelled from the crystals by heat, and the monohydrate is left, BaH_2O_2, of density 4·495; it fuses at a heat above redness, and is not decomposed into baric oxide and water even at a very high temperature. Baric hydrate is sparingly soluble in alcohol.

(689) **SULPHIDES OF BARIUM.**—Of these the most important is the *protosulphide*, $BaS = 169$. The preparation of this substance from baric sulphate presents some interest to the chemist, for it enables him to obtain with ease the soluble salts of barium from its insoluble sulphate, the baric compound which occurs most abundantly in nature. In order to prepare the sulphide, either the native or the artificial sulphate is reduced to a very fine powder, and intimately mixed with an equal weight of starch or flour, or with one-tenth of its weight of powdered charcoal; this is made up into a paste with oil, and introduced into a crucible lined with charcoal: the cover is luted on, and the crucible and its contents are exposed for an hour to an intense heat. By this treatment most of the baric sulphate is deoxidized, carbonic oxide escaping, whilst baric sulphide remains: $BaSO_4 + 4C = BaS + 4CO$. When the mass thus obtained is treated with successive small quantities of boiling water, the sulphide is decomposed; the first portions of the solution have a yellow colour, owing to the formation of sulphhydrate of barium, which absorbs oxygen and becomes partially converted into baric disulphide, whilst the latter washings contain gradually increasing quantities of baric hydrate; $2BaS + 2OH_2 = BaH_2S_2 + BaH_2O_2$, and $2BaH_2S_2 + O_2 = 2BaS_2 + 2OH_2$; but if the mass be treated at once with a sufficient quantity of boiling water, the whole of the sulphide is dissolved and is deposited again as the solution cools in colourless transparent crystals, with $6OH_2$. When treated with an acid such as hydrochloric acid, the baric sulphide

is decomposed, and the corresponding barium salt is formed, whilst sulphuretted hydrogen escapes; for instance, $BaS + 2HCl = BaCl_2 + SH_2$. Baric sulphhydrate is also produced when sulphuretted hydrogen is passed through water in which freshly precipitated baric carbonate is suspended: the action is slow, however, and incomplete unless a comparatively large quantity of water be employed.

(690) **BARIC SULPHATE**, or *Sulphate of barium:* $BaSO_4 = 233$; *Density*, 4·59: *Comp. in* 100 *parts*, BaO, 65·66; SO_3, 34·34. —This is the principal native mineral of baryta. It occurs in the mountain limestone in large veins, and is found accompanying the ores of lead and other metals. It is met with both massive and crystallized, in modifications of the right rhombic prism. The name 'baryta' is derived from βαρὺς, heavy, in allusion to the high specific gravity of this compound, which is about 4·6. It is insoluble in water, and in all the acids except boiling concentrated sulphuric acid: as its solution in this acid cools, crystals of the sulphate are deposited. De Senarmont found that when the recently precipitated sulphate is heated to 250° (482° F.), for 60 hours in a sealed tube, with dilute hydrochloric acid, or with a solution of hydric sodic carbonate (bicarbonate), microscopic crystals of the same form as those of the native baric sulphate are deposited upon the sides of the tube. The formation of similar crystals may be observed when a very dilute solution of baric chloride (1 part in 10,000) is mixed with a small proportion of sulphuric acid at ordinary temperatures. At a bright red heat the sulphate fuses to a white enamel: and by boiling the powdered baric sulphate with either potassic or sodic carbonate, or, more rapidly by fusing it with either of these salts, the artificial sulphate is partially converted into the carbonate. Baric sulphate may be easily obtained as a heavy white powder by precipitating a solution of a baric salt with any soluble sulphate. If nitric acid or a nitrate be present in the solution, the precipitate carries down with it a portion of the nitrate, and this can only be removed by long washing with boiling water. Baric sulphate is used as a *permanent white* by artists in water colours. It is also employed for adulterating white lead, but when ground with oil, it becomes partially transparent, and impairs the opacity of the lead pigment.

(691) **BARIC NITRATE**, or *Nitrate of barium* ($Ba2NO_3 = 261$; *Density*, 3·284; *Comp. in* 100 *parts*, BaO, 58·62; N_2O_5, 41·38) crystallizes in anhydrous octohedra, when a solution of the baric carbonate in nitric acid is evaporated. It is insoluble

in alcohol and requires eight or ten times its weight of cold water, and 3 of boiling water, for solution. Nitric acid precipitates it in crystals from its solution, unless very dilute: when heated, it first decrepitates strongly, and afterwards fuses; at a high temperature the whole of the acid is expelled, with an appearance of ebullition caused by the escape of oxygen and nitrogen, pure baric oxide remaining in the crucible.

(692) **BARIC CHLORATE,** $Ba.2ClO_3 = 304$.—This salt may be prepared from potassic chlorate by decomposing it with a slight excess of hydrofluoric acid, filtering from the sparingly soluble potassic fluosilicate, neutralizing with baric carbonate, and then adding a little baryta water to precipitate any iron, &c., that may be present. On concentrating the filtered solution the baric chlorate crystallizes out and may be purified by recrystallization. Advantage may also be taken of the sparing solubility of potassic alum for the preparation of baric chlorate: 1 mol. of aluminic sulphate, 2 of finely powdered potassic chlorate, and 1 of sulphuric acid diluted with water, are thoroughly mixed and heated for a short time: on cooling, the crystalline mass of potassic alum is washed with alcohol, the solution of chloric acid neutralized with baryta, filtered, and after removal of the alcohol by distillation, the liquid is concentrated until the baric salt crystallizes out on cooling.

(693) **BARIC CARBONATE,** or *Carbonate of barium:* $BaCO_3 = 197$; *Density,* 4·3; *Comp. in* 100 *parts,* BaO, 77·67; CO_2, 22·33.—This compound forms the mineral called *witherite:* it occurs, both massive and crystallized, usually in six-sided prisms terminated by six-sided pyramids. It is abundant in the lead-veins in the north of England, and is also found in Styria and in Siberia. It is easily prepared artificially by precipitating a barium salt by the carbonate of one of the alkali-metals; it then forms a white powder, which is very sparingly soluble in pure water, and is insoluble in water charged with saline matter: an aqueous solution of carbonic acid dissolves it rather freely. Freshly precipitated baric carbonate is converted into sulphate, if suspended in a solution of potassic or sodic sulphate, in the cold, and frequently agitated; but if baric sulphate be boiled with a carbonate of one of the alkali-metals, carbonate of barium and sulphate of the alkali-metal are produced. Ignition of the carbonate does not expel the carbonic anhydride, but if it be mixed with charcoal and intensely ignited, it is partially decomposed; pure baryta is obtained, and may be dissolved out with water. If mixed with an equal weight of calcic carbonate, baric carbonate is decomposed without much difficulty when ignited in a current of steam, a mixture of baric and calcic hydrates being formed; the baric hydrate may then be dissolved out of the mixture by water.

Baric carbonate is now manufactured to some extent for use as a substitute for a portion of the alkali and oxide of lead in the making of plate and flint glass: the baric silicate which is formed fuses and becomes incorporated with the other silicates. The carbonate is prepared for this purpose from the sulphate, which is reduced to the form of sulphide by ignition with carbonaceous matter: the sulphide is then dissolved in water, and decomposed by a current of carbonic anhydride, which precipitates the baric carbonate as a fine white powder.

(694) **Characters of the Salts of Barium.**—The barium salts with colourless acids are colourless. The carbonate and all the soluble salts act as powerful poisons, and have an acrid, disagreeable taste. The best antidote when they have been taken internally is sodic or magnesic sulphate.

Barium salts when in solution are easily recognized by giving with *sulphuric acid* a white precipitate of baric sulphate, which is insoluble in the acids. Barium is, for the purposes of analysis, usually estimated in the form of sulphate; 100 parts correspond to 65·66 of BaO and 34·34 of SO_3. The presence of citrate of sodium or of ammonium prevents the precipitation of baric sulphate in neutral and alkaline solutions; but these salts do not redissolve the baric sulphate after it has once been deposited. On acidulating with hydrochloric acid the solution containing the citrates, baric sulphate is precipitated in the usual manner (Spiller).

With *potassic* or *sodic carbonate* a white precipitate of baric carbonate is produced in solutions which contain barium. *Ammonic hydric sulphide* gives no precipitate in such solutions. *Hydric disodic phosphate* gives a white precipitate which is soluble in dilute nitric or hydrochloric acid. Soluble barium salts, when mingled with alcohol, tinge its flame of a yellowish-green colour. In the spectroscope, the spectrum of the barium salts is distinguished by a remarkable series of bright bands in the green, with fainter bands in the red. (Part I. fig. 83, *Ba*, page 196). Barium salts are distinguished from those of strontium by forming an insoluble baric silicofluoride when mixed with *silicofluoric acid*; and by yielding no immediate precipitate with *oxalic acid*, but the mixture on standing deposits tufts of acicular crystals of acid oxalate of barium. A solution of *sodic thiosulphate* (*hyposulphite*) occasions a crystalline precipitate of the sparingly soluble baric thiosulphate (hyposulphite).

§ II. STRONTIUM: $Sr'' = 87{\cdot}6$. *Density*, 2·54.

(695) **STRONTIUM** is an element much less abundantly diffused than barium, which it closely resembles in properties. It is found both as carbonate and as sulphate, and is procured in the metallic state in the same way as barium, to which it bears a relation similar to that existing between potassium and sodium. Strontium is a malleable metal of a bright yellow colour. When heated in the air, it burns with a crimson flame, emitting sparks. Water is decomposed by it with evolution of hydrogen: dilute nitric acid dissolves it, but the concentrated acid is almost without action even when boiled with it.

(696) **STRONTIC CHLORIDE**, or *Chloride of strontium*: $SrCl_2.6OH_2 = 158{\cdot}6 + 108$; *Density, anhydrous*, 2·96; *cryst.* 1·603.—It crystallizes in slightly deliquescent needles, which require less than their weight of cold water for solution; alcohol dissolves it, and the solution burns with a crimson flame. Strontic chloride is rendered anhydrous by a moderate heat; if strongly heated it fuses.

(697) **STRONTIC SILICOFLUORIDE**, $SrF_2.SiF_4 = 229{\cdot}6$, is prepared by adding hydrofluosilicic acid to a salt of strontium: it is tolerably soluble in water, thus furnishing a means of distinguishing the compounds of barium from those of strontium.

(698) **STRONTIC OXIDE**, or *Strontia*; $SrO = 103{\cdot}6$: *Density*, 4·611.—This may be obtained from its nitrate by ignition. When mixed with water it slakes, and forms a crystalline hydrate, $SrH_2O_2.8OH_2$; *density*, 1·396: these crystals require 50 times their weight of cold and 24 of boiling water for solution; the water of crystallization, $8OH_2$, is easily expelled by heat, the remaining molecule requiring a much higher temperature for its expulsion; at a red heat the latter hydrate fuses, furnishing a mass of density 3·625: both the hydrate and its solution absorb carbonic anhydride rapidly from the air. Hydrated *Strontic peroxide* is precipitated in crystalline scales having the composition $SrO_2.8OH_2$ when an aqueous solution of sodic peroxide is added to a solution of strontic chloride. At 100° (212° F.) it loses its water and leaves strontic peroxide, SrO_2, as a white powder (Conroy).

(699) **STRONTIC SULPHATE**, or *Sulphate of strontium*: $SrSO_4 = 183{\cdot}6$; *Density*, 3·9; *Comp. in* 100 *parts*, SrO, 56·43; SO_3, 43·57.—This substance is found crystallized in rhombic prisms isomorphous with those of baric sulphate; it is, however, easily distinguished from it by its lower density. Many specimens of this mineral have a delicate blue tint, whence it derives its mineralogical name of *celestine*: it often contains crystals of native sulphur. Strontic sulphate is very sparingly soluble in water, but is taken up by boiling sulphuric acid, and is soluble to some extent in a solution of sodic chloride. It may be formed by mixing a solution of a sulphate with a solution of a strontium salt.

(700) **STRONTIC NITRATE**, or *Nitrate of strontium*: $Sr2NO_3 = 211{\cdot}6$; *Density*, 2·305.—This salt crystallizes from hot concentrated solutions in anhydrous octohedra, which are soluble in 5 parts of cold water and half their weight of boiling water; by crystallizing it at a low temperature it may be obtained in efflorescent monoclinic crystals with $4OH_2$. If strongly heated, it decrepitates, and at a higher temperature is decomposed leaving pure strontia, whilst oxygen and nitrogen are evolved. It gives a splendid crimson colour to flame, and is largely used by the makers of fireworks for that purpose, being usually prepared by reducing the native sulphate to sulphide by heating it with charcoal, dissolving the sulphide in water, and decomposing it with dilute nitric acid. It crystallizes best from an acid solution. A mixture of 40 parts of strontic nitrate with from 5 to 10 of potassic chlorate, 13 of sulphur, and 4 of antimonious sulphide, deflagrates with a magnificent red colour; the mixture is dangerous both to prepare and to preserve, having more than once been the occasion of frightful accidents to the manufacturers, from becoming spontaneously ignited. Strontic nitrate is insoluble in alcohol.

(701) **STRONTIC CARBONATE**; $SrCO_3 = 147{\cdot}6$; *Density*, 3·65; *Comp. in* 100 *parts*, SrO, 70·19; CO_2, 29·81.—This compound forms the *strontianite* of mineralogists; it occurs both massive and crystallized, near Strontian in Argyleshire, hence the name 'strontia.' Mere ignition is insufficient to decompose this salt. It is scarcely soluble in water, but is dissolved by a solution of carbonic acid. It may be prepared artificially by precipitating a strontium salt with ammonium carbonate or the carbonate of one of the alkali-metals.

(702) **Characters of the Strontium Salts.**—The strontium salts with colourless acids are all colourless: they have a bitter acrid taste, but are not poisonous like those of barium. They are distinguished *before the blowpipe* by the red colour which they communicate to the flame; this is resolved by the spectroscope into several bright bands in the red and orange part of the spectrum, and a brilliant band in the blue. (Fig. 83, *Sr*, Part I. p. 196.) The flame of strontium to the unaided eye seems to have the same colour as that of lithium, but the spectra of the two are very different. Reagents produce with strontium salts the same effects as with those of barium, excepting that neither *silicofluoric acid* nor *sodic thiosulphate* (*hyposulphite*) yields any precipitate in the solutions of strontium salts. *Oxalic acid* gives an immediate turbidity in them. The compounds of

strontium are distinguished from those of calcium by the gradual formation of a white precipitate on agitation after the addition of a solution of *calcic sulphate*. Strontic sulphate is used for determining the amount of strontia in analysis; 100 parts of it correspond to 56·43 of strontia.

§ III. CALCIUM: Ca″=40.

(703) **CALCIUM**; *Density*, 1·578.—This metal forms one of the most abundant and important constituents of the crust of the globe. It derives its name from *calx*, lime, of which earth it is the metallic basis. Calcium occurs in nature in combination with fluorine, forming the different varieties of fluor-spar; it is still more abundant in the various forms of calcic carbonate; and it is also met with in large quantities as gypsum, which is a hydrated calcic sulphate.

Calcium was obtained by Matthiessen (*Jour. Chem. Soc.*, 1855, viii. 27) by the electrolytic decomposition of a mixture consisting of 2 molecules of calcic chloride and 1 of strontic chloride. The mass may be fused in a Hessian crucible, in the centre of which is placed a porous tube filled with the same mixture, and into this an iron wire passed through the stem of a tobacco-pipe is inserted; this wire is connected with the platinode of the battery, the zincode of which consists of a plate of sheet-iron bent into a cylindrical form, and immersed in the melted mass exterior to the porous tube: the calcium is reduced, and preserved from oxidation by so regulating the heat that a film of solidified salt shall form upon the surface of the mixture in the porous cell. Lies Bodart obtains it still more easily by fusing calcic iodide with an equivalent quantity of sodium in an iron crucible having the lid screwed down, as the reaction does not take place at the ordinary atmospheric pressure.

Calcium is not yellow as usually stated, but, according to Frey (*Ann. Chem. Pharm.*, 1876, clxxxiii. 367), of a greyish white, somewhat like aluminium; moreover, it is not malleable and cannot be drawn into wire: in hardness it is intermediate between sodium and lead. It melts at a red heat. At ordinary temperatures it tarnishes within a day or two, even in dry air, and in the presence of moisture it is slowly oxidized. When heated to redness on platinum foil, it burns with a brilliant scintillating white light. It readily amalgamates with mercury: when heated in chlorine, or in the vapour of bromine, iodine, or sulphur, it burns with an extremely vivid light. Water is rapidly decomposed by calcium, calcic hydrate being formed and hydrogen evolved. Concentrated nitric acid does not attack the metal until heated to the boiling-point, although the diluted acid dissolves it rapidly. Matthiessen found that calcic chloride is not decomposed by heating it with potassium or sodium; and he concludes that the properties formerly assigned to calcium were really those of a mixture of potassium with aluminium and silicon.

(704) **CALCIC CHLORIDE**, or *Chloride of calcium*: $CaCl_2.6OH_2 = 111 + 108$; *Density, fused*, 2·485; *cryst.* 1·680; *Comp. in* 100 *parts*, Ca, 36·03; Cl, 63·97.—This salt is obtained as a secondary product in the manufacture of ammonic carbonate

from the chloride; it may be prepared by dissolving chalk in excess in hydrochloric acid, adding a little lime to precipitate iron, &c., filtering, evaporating to dryness, and fusing the residue at a red heat. Under these circumstances, a small portion of the chlorine is displaced by the oxygen of the air, so that the mass has an alkaline reaction, owing to the presence of lime. By evaporation of its solution the chloride may be obtained in striated prismatic six-sided crystals with $6OH_2$, which fuse at 29° (84°·2 F.). In this form it produces great depression of temperature when dissolved in water, and if mixed with snow it furnishes a powerful freezing mixture. If the hydrated salt be exposed to a temperature of 150° (302° F.) for a considerable time, it forms a porous mass which still retains $2OH_2$; in this state it is well adapted for the desiccation of gases. Calcic chloride is extremely deliquescent and soluble, the solution saturated at 29° (84°·2 F.) containing half its weight of $CaCl_2$. A saturated solution of the salt boils at 179°·5 (355° F.), and is sometimes employed where a steady temperature, not exceeding this point, is required. It is soluble in alcohol, and may be obtained from its alcoholic solution crystallized in rectangular plates containing 4 molecules of alcohol, and having the formula $CaCl_2.4C_2H_6O$: a corresponding hydrate, $CaCl_2.4OH_2$, may be obtained in large plates by cooling a hot solution containing 55 per cent. $CaCl_2$ to a temperature of 15° (59° F.). Calcic chloride absorbs ammonia rapidly, and forms a compound with 8 molecules of the gas. A solution of the chloride, if boiled with quicklime and filtered whilst hot, deposits long, flat, thin crystals of a hydrated oxychloride, $CaCl_2.3CaO.16OH_2$, which is decomposed both by water and alcohol. Grimshaw (*Chem. News*, 1874, xxx. 280) makes the formula $CaO.CaOHCl.7OH_2$.

(705) **CALCIC BROMIDE**; $CaBr_2$.—Silky needles of the hydrated bromide are obtained on evaporating a solution of calcic hydrate in aqueous hydrobromic acid.

(706) **CALCIC IODIDE**; CaI_2.—This is a soluble colourless compound, which may be obtained by dissolving chalk in hydriodic acid, and evaporating the solution rapidly to dryness in a vessel from which the air is excluded, or by adding iodine to mixed calcic sulphite and hydrate suspended in water; arsenious acid may be substituted for the calcic sulphite, in which case insoluble calcic arseniate is formed.

(707) **CALCIC FLUORIDE**, or *Fluoride of calcium*; $CaF_2 = 78$; *Density*, 3·14; *Comp. in* 100 *parts*, Ca, 51·28; F, 48·72.—This is an abundant mineral, well known as *fluor-spar*, which occurs either massive, or crystallized in forms allied to the cube. It is found accompanying the lead-veins in Cumberland, Derbyshire,

and Cornwall, and is met with in a variety of other localities, of various colours, most frequently blue, green, or white. Fluor-spar is the principal source from which the compounds of fluorine are obtained. Calcic fluoride, in minute quantity, is found in sea-water, and in many springs: it is a never-failing companion of calcic phosphate in the bones and teeth of animals, and indeed is always found to accompany calcic phosphate in the mineral kingdom also, in small but variable quantities. Many varieties of fluor-spar, when gently heated, become phosphorescent, emitting a pale green or violet light; if heated more strongly, the crystals decrepitate, and each fragment becomes enveloped for a few seconds in a beautiful halo of light. It loses this property after having been once heated, but it may be restored by passing over the mineral a current of electricity of high tension, such as that from a Leyden jar, or an induction coil; a phosphorescent fluor, dissolved in hydrochloric acid and precipitated by ammonia, retains its power of emitting light when heated, but if it had been previously heated sufficiently to destroy the phosphorescence, this property is not restored by solution and reprecipitation. Many other fluorides besides that of calcium, when in the crystalline state, possess the curious property of phosphorescence.

Powdered fluor-spar, if mixed with sulphuric acid at a low temperature, forms a transparent, viscous mass, from which fumes of hydrofluoric acid are evolved by heating it to 40° (104° F.). Fluor-spar undergoes no change when heated with sulphuric anhydride, but with boracic anhydride it yields calcic diborate and boric trifluoride; $3CaF_2 + 4B_2O_3 = 3(Ca2BO_2) + 2BF_3$. Hydrochloric acid dissolves it in small quantity. If heated in a current of chlorine, a gas is expelled which corrodes glass; it is probably a chloride of fluorine. When fluor-spar is fused with the hydrated alkalies, it undergoes no change: with the carbonates of the alkali-metals, fluoride of the alkali-metal and calcic carbonate are formed. If heated with calcic sulphate, it fuses and forms a glass which is transparent while hot, but enamel-white when cold. In proper proportions it often forms a valuable flux in smelting the ores of various metals, and hence the name *fluor* is derived, but it requires rather an elevated temperature to fuse it when heated without any admixture.

(708) **LIME, or CALCIC OXIDE**; CaO = 56; *Density*, 3·18; *Comp. in* 100 *parts*, Ca, 71·43; O, 28·57.—Calcium forms two oxides, one of which, viz., lime, has been known from time immemorial. It is obtained in a state of purity by heating pure calcic carbonate (719) to full redness; this carbonate occurs very nearly pure either in black or in Carrara marble, which if burnt for an hour or two in an open fire—or better still, in a crucible with a hole at the bottom—yields lime very nearly free from foreign matters. For commercial purposes, common limestone, which is an impure calcic carbonate, is burned in a kiln, the

cavity of which is usually egg-shaped. Over the fire-grate an arch is formed with lumps of limestone, and the kiln is filled up with smaller fragments, the fire is then kindled below, and kept up continuously for three days and nights; the kiln is then allowed to cool, the lime is removed, and a fresh charge introduced. A better method is that known as the continuous process. The kiln in this case is in the form of an inverted truncated cone: it is charged with alternate layers of coal and limestone, and the fire is kindled. The lime, as it is burned, gradually sinks down, and is removed by openings at the base of the furnace, and a fresh supply of coal and limestone is supplied at the top of the kiln. The limestone should not be too dry; that which has been quarried recently answers best. In damp weather, too, the operation succeeds better than in a dry state of the atmosphere; indeed, the process is facilitated by injecting steam into the kiln, although in practice the advantage which is gained does not compensate for the increased expense and trouble. In the presence of aqueous vapour an interchange between the steam and the carbonic anhydride of the limestone appears to be effected, and calcic hydrate is formed; but the hydrate which is produced is quickly decomposed again.

Pure lime, or *quicklime*, is a white caustic powder which does not fuse even in the intense heat of the oxyhydrogen flame but emits a brilliant white light when thus ignited, as is seen in its application to the Drummond light. The extreme infusibility of lime has led Deville to employ it as a material for lining crucibles which are to be exposed to very intense heat, and also for the construction of a furnace for use with the oxyhydrogen blowpipe.

(709) **CALCIC PEROXIDE.**—A hydrated calcic peroxide, $CaO_2.8OH_2$, is precipitated on adding excess of lime water to a solution of sodic peroxide, which has been previously neutralized with nitric acid. When dried at 100° (212° F.) it loses its water of crystallization, leaving the anhydrous peroxide, CaO_2, as a pale buff-coloured powder (Conroy).

(710) **CALCIC HYDRATE,** *Hydrate of lime,* or *Slaked lime;* $CaH_2O_2=74$; *Density,* 2·078; *Comp. in* 100 *parts,* CaO, 75·68; OH_2, 24·32.—When water is poured upon lime, it swells up and enters into combination with the water; if the proportion of water be not too great, a light dry powder is formed, attended with a powerful development of heat: so great is this that fires have several times been traced to this source. The hydrate which is formed is a definite compound of 1 molecule of water with 1 of lime. Lime, when exposed to the air, slowly attracts both water

and carbonic anhydride, and as the result of this action it falls to powder, and becomes what is termed *air slaked*; in this case a compound is gradually formed, which is by some chemists regarded as a combination of a molecule of calcic carbonate with one of hydrate ($CaCO_3.CaH_2O_2$).

Lime is soluble in about 780 parts of cold water, yielding a solution which is known as lime-water; it is, however, less soluble in hot than in cold water, so that if lime-water saturated in the cold be raised to the boiling point, half the lime is deposited. Lime is much more soluble in a solution of cane sugar than it is in water; the liquid in this case also becomes turbid when heated, but clears again as it cools. Lime-water is much employed as a test for the presence of carbonic acid, which instantly renders it turbid: it has a distinctly alkaline reaction, and an acrid taste: by evaporating it *in vacuo*, Gay-Lussac obtained calcic hydrate crystallized in hexahedral plates. Calcic hydrate is decomposed by a red heat, and pure lime remains.

Milk of lime is merely hydrated lime diffused through water: in slaking lime for its preparation, and, indeed, generally where small quantities of the hydrate are required in a fine state of subdivision, it is best to use boiling water in quantity nearly equal to twice the weight of the lime, care must, however, be taken in slaking it in this way, otherwise the action is so violent that portions of the mixture are apt to be violently projected from the vessel; the powder may afterwards be readily diffused through cold water.

(711) **Mortars and Cements.**—The great consumption of lime in the arts is for the purpose of making mortars and cements. Pure lime, when made into a paste with water, forms a somewhat plastic mass, which sets into a solid as it dries, but gradually cracks and falls to pieces. It does not possess sufficient cohesion to be used alone as a mortar; to remedy this defect and to prevent the shrinking of the mass, the addition of sand is found to be necessary. Ordinary mortar is prepared by mixing 1 part of lime into a thin paste with water, and adding 3 or 4 parts of sharp sand, of tolerable fineness: the materials are then thoroughly incorporated, and passed through a sieve to separate lumps of imperfectly burned lime: a suitable quantity of water is afterwards worked into it, and it is then applied in a thin layer to the surfaces of the stones and bricks which are to be united. The bricks or stones are moistened with water before applying the mortar, in order that they may not absorb the water from the mortar too rapidly. The completeness of the subsequent

hardening of the mortar depends mainly upon the thorough intermixture of the lime and sand.

The theory of the hardening of mortar is obscure. The mortar gradually becomes dry upon its surface, and at the same time it absorbs carbonic anhydride from the air; but this change is rarely complete, for the central portions, after a lapse of many ages, are still found to contain free lime in abundance: mortar taken by Dr. Malcolmson from the Great Pyramid, was still found to contain a large proportion of lime as hydrate. A gradual combination also takes place between the lime and the silica of the sand: each grain of sand thus becomes superficially converted into a hydrated calcic silicate, forming a compound which by degrees acquires considerable hardness, and contributes greatly to the solidification of the mortar. All old mortar, when treated with an acid, yields a small proportion of gelatinous silica. A mixture of calcic carbonate with the lime appears to set harder than pure lime only; so that for many purposes lime which has been slaked by exposure to the air, and contains a considerable proportion of carbonate, is preferred to that slaked rapidly by water.

Limestones vary greatly in composition; being rocks of sedimentary origin, they are not pure chemical compounds, but consist of a mixture of various bodies, in which calcic carbonate is the principal ingredient. The different varieties of limestone are distinguished according to the nature of the most important of these admixtures: a limestone, for example, is described as magnesian, argillaceous, ferruginous, sandy, or bituminous, according as it is characterized by the presence of magnesic carbonate, clay, ferric oxide, sand, or bituminous matter. These different limestones, when burned, yield lime of very different qualities, as is shown by the action of water upon the lime produced. The purer the lime, the more quickly does it combine with water when mixed with it. Such pure limes are technically termed *rich* or *fat* limes; when the amount of impurities present does not exceed 10 per cent., they slake rapidly, swelling up and increasing greatly in bulk; they become extremely hot, and yield a soft, fine, dense paste; whilst those which contain much magnesia, silica, or alumina, slake slowly, emit but little heat, and are techically termed *poor*.

In slaking for mortar, a fine smooth paste is required: in order to secure this condition, the slaking should be effected quickly, with about 3 parts of water to 1 of lime; the mass, if composed of a fat lime, then swells to between three and four

times its former bulk: if too little water be used, a crystalline granular hydrate is formed.

The temperature required for burning lime varies with the composition of the limestone. When a siliceous limestone is burnt, the silica combines with the lime if the temperature be too high and be too suddenly raised, and a coating of silicate forms on the surface of the mass, which becomes partially vitrified. Such lime slakes very imperfectly, and is said to be *dead burnt*. If ordinary quicklime be mixed with a small quantity of calcic sulphate, or if it be reburnt at a dull red heat in an atmosphere containing a small proportion of sulphurous anhydride, it acquires the property of setting slowly like stucco when mixed with cold water, but if boiling water be used it slakes like common lime. Lime so prepared is known as *Scott's cement*.

(712) **Hydraulic Mortars.**—Ordinary mortar, when placed in water, becomes gradually softened and disintegrated, whilst the lime is dissolved away. It cannot therefore be used for subaqueous constructions. Some poor limes, however, which contain from 15 to 35 per cent. of finely divided silica or clay, form what are termed *hydraulic limes:* when mixed with a due proportion of sand (from 1·5 to 1·8 times their weight) they furnish a mortar which possesses the valuable property of hardening under water. These limes may be artificially imitated by mixing with the lime a due proportion of clay not too strongly burnt. At Puzzuoli, near Naples, a porous volcanic material, which has received the name of *puzzuolana,* is found. This substance, when powdered and mixed with ordinary lime, confers upon it the property of yielding an excellent hydraulic mortar, which was employed by the Romans in many of their buildings, in which it is still in perfect preservation, having resisted the ravages of time more perfectly than the bricks which it was used to cement. It is found that a puzzuolana which is easily attacked by sulphuric acid is more effective than one which resists the action of the acid. The comparative value of a puzzuolana may also be roughly and rapidly estimated by taking a given measure of lime-water, and agitating it with successive small quantities of finely powdered puzzuolana until the alkaline reaction disappears; the puzzuolana combines with the lime and abstracts it from the water. The smaller the quantity of the powder required, the more active are its hydraulic powers. Puzzuolana consists chiefly of silicates of aluminium, calcium, and sodium.

Many other substances, when added to lime, confer upon it hydraulic properties to a greater or less extent. Gelatinous silica shows this power slightly, and a mixture of hydrated silica with freshly precipitated alumina or magnesia shows it in a remarkable degree. Sand, ferric oxide, and black oxide of manganese, are

destitute of this property. From a knowledge of these facts it is easy to convert ordinary lime into one possessed of hydraulic properties. Clay is an aluminic silicate; when it is heated with lime, decomposition occurs, the alumina is set free, and calcic silicate is formed. The materials are in this way reduced to a condition suitable for use as a hydraulic cement, without the addition of sand; but great care is required in regulating the temperature. If it be allowed to rise too high, partial vitrification occurs, which impairs the tendency of the cement to combine with water; whilst, on the other hand, if the heat be insufficient, the alumina is not liberated from its combination with the silica. The immediate cause of the solidification of these hydraulic limes appears, according to the experiments of Fremy and others, to be the formation of a hydrated compound of lime with the alumina, which is very hard, and insoluble in water.

Hydraulic limes do not slake with any considerable emission of heat when moistened; they absorb the water without increasing much in bulk, and form a paste of small plasticity. In order that a hydraulic mortar may harden properly, it must not be submerged until it begins to set; it should then be kept moist until it is quite hard, otherwise it will always remain porous.

The manufacture of artificial hydraulic cement was first established upon sound principles by Vicat. He proceeds thus in its preparation:—Four parts of chalk are ground and levigated in water with 1 part of clay, so as to obtain a very intimate mixture of the materials, which are allowed to subside, moulded into blocks, dried, and calcined at a carefully regulated temperature. *Portland cement* is a hydraulic cement similar to the above. It is made from clay obtained in the valley of the Medway, and from chalk found in the same neighbourhood: it derives its name from the circumstance that in colour, when dry, it resembles Portland stone. It is prepared by thoroughly grinding the clay and chalk with water, allowing them to subside, then drying and burning the mixture until it undergoes slight vitrification; the mass is again ground, and when mixed with a proper proportion of water, it forms a cement which possesses great hardness and tenacity; it expands as it solidifies. In preparing this cement, if the lime be first burned and then mixed with clay and reburned, it does not require more than a full red heat to produce a good cement.

The rapidity with which these different kinds of hydraulic lime set, varies considerably with their composition. If the clay does not exceed 10 or 12 per cent. of the weight of the original limestone, the mortar requires several weeks to harden. If the clay amounts to from 15 to 25 per cent., it sets in two or three days, and if from 25 to 35 per cent. of clay is present, the solidification occurs in a few hours. The substance to which the term *Roman cement* is now applied is a lime of this latter description. Roman cement is extensively prepared from nodules of septaria

which occur in the valley of the Thames. It sets in a few hours after the mixture with water has been effected, and it soon rivals stone in hardness. According to Meyer, the composition of the nodules employed in the preparation of the cement is the following:

Matter soluble in acid 76·0	Calcic carbonate ...	66·99
	Magnesic carbonate..	1·67
	Ferrous carbonate...	6·95
	Alumina	0·39
Insoluble in acid (clay) 23·305	Silica	16·89
	Alumina	4·32
	Ferric oxide	1·72
	Lime	0·005
	Magnesia	0·37

The cement obtained from the neighbourhood of Boulogne is almost identical in composition with the foregoing; and similar materials have been obtained in other countries, particularly in the beds of the Jurassic formation. The presence of calcic sulphate, even in comparatively small quantity, is very injurious to the quality of cement, as it becomes dead burnt in the process of manufacture, and then by slowly taking up water after the cement is set expands and causes it to crumble.

Concrete is a mixture of hydraulic mortar with small pebbles coarsely broken.

(713) **Other Uses of Lime.**—Lime is also largely employed as a manure, and it is particularly valuable upon very rich vegetable soils, such as those formed over peat bogs: its effects in these cases are partly due to the decomposition of the organic matter, which it renders soluble and capable of assimilation, whilst the lime itself is converted into carbonate. It has been found that limestone containing much magnesic carbonate yields a lime unsuited to agricultural purposes; this has been attributed to the fact that magnesia absorbs carbonic anhydride much more slowly than lime, and remains caustic for a longer period, in which state it appears to be injurious to the tender shoots of young plants.

The great facility with which lime is converted into calcic carbonate renders it a valuable material for decomposing the potassic and sodic carbonates, when it is desired to prepare the corresponding hydrates. The attraction of lime for water furnishes a ready means of removing this liquid from many substances which obstinately retain it, such as alcohol. Slaked lime is employed as a direct chemical agent in the purification of coal-gas, and as a means of loosening the epidermis, and facilitating the removal of the hair from hides, as a preliminary to the process of tanning.

(714) **SULPHIDES OF CALCIUM.**—Calcium forms several compounds with sulphur, some of which are soluble.

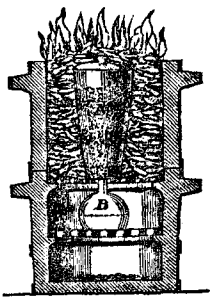
Calcic Sulphide, $CaS=72$, is prepared by decomposing a mixture of calcic sulphate and charcoal by heat as directed for preparing baric sulphide. It is insoluble in cold water, but when treated with boiling water in small proportion is converted into calcic hydrate, and a soluble calcic dihydric disulphide, $2CaS+2OH_2=CaH_2S_2+CaH_2O_2$. Calcic sulphide is phosphorescent when freshly prepared. This property was first observed by Canton, in an impure calcic sulphide, which he obtained by calcining oyster-shells in an open fire for half an hour, then selecting the whitest and largest portions, and packing them with one-third of their weight of flowers of sulphur in a crucible with a luted cover; this was heated strongly for an hour: when cold, the crucible was broken, and the whitest pieces were placed in well-closed bottles.

Calcic sulphide forms one of the principal constituents in the soda waste of the alkali maker. When exposed to the air in a moist state it absorbs oxygen and furnishes calcic thiosulphate (hyposulphite) in large quantity: $2CaS+OH_2+2O_2=CaH_2O_2+CaS_2O_3$; this can readily be converted into the corresponding sodic salt by decomposing it with sodic carbonate (433).

By boiling slaked lime with excess of sulphur, *calcic pentasulphide* is obtained; calcic thiosulphate (hyposulphite) being formed at the same time: $3CaO+6S_2=2CaS_5+CaS_2O_3$.

(715) **CALCIC PHOSPHIDE**; Ca_2P_2 P = 142.—This compound presents some interest, from its affording the most convenient source of some of the phosphides of hydrogen (502). It is prepared by distilling phosphorus over lime heated to low redness: a mixture of calcic phosphide and pyrophosphate is the result, $14P+14CaO=5Ca_2P_2+2Ca_2P_2O_7$ (P. Thénard). The most convenient method of conducting the operation is shown in fig. 347. In the lower part of a narrow deep crucible, A, a hole is drilled for the reception of the neck of a flask, B, which is luted into the aperture; a quantity of dry phosphorus is placed in the flask, and the crucible is filled with quicklime, broken into fragments of about the size of a hazel-nut; a lid is then luted upon the top of the crucible. Time having been given for the luting to become dry, the upper part of the crucible is raised to a red heat as quickly as possible, by surrounding it with ignited charcoal, the lower part of the furnace having been filled with cold charcoal, to prevent the heat from reaching the phosphorus too rapidly; the phosphorus becomes gradually volatilized as the heat reaches it. If the heat be too high, the phosphorus distils over without combining with the calcium.

FIG. 347.



Calcic phosphide when prepared in this manner forms an anhydrous mass of a dull red colour, hard enough to strike

fire with steel: it experiences no change in dry air or in oxygen at the ordinary temperature. At a high temperature it becomes partially decomposed by oxygen, chlorine, or hydrochloric acid; in a moist atmosphere it slakes, emits phosphuretted hydrogen, and crumbles to a brown powder. This powder, when thrown into water, or heated to 100° (212° F.), evolves phosphuretted hydrogen, which is not self-lighting, and is mixed with free hydrogen.

Calcic phosphide, in its unslaked form, is decomposed when thrown into water, and the phosphuretted hydrogen gas evolved, takes fire in the manner already described (501): dilute acids decompose it still more readily.

(716) **CALCIC DISILICIDE,** or *Silicide of calcium;* Si_2Ca.—Wöhler (*Ann. Chem. Pharm.*, 1863, cxxvii. 257), in order to prepare this singular compound, directs 20 grams of graphitoid silicon to be finely powdered and intimately mixed with 200 grams of calcic chloride in a hot mortar, and to be rapidly shaken up in a wide-mouthed bottle with 23 grams of sodium cut into small pieces: meantime a Hessian crucible is to be brought to a full red heat in a good wind-furnace; a little fused common salt is to be thrown into the crucible, then 23 grams of sodium, and finally the mixture of silicon, sodium and calcic chloride; the whole being covered with a layer of pulverized fused sodic chloride: after the cover is put on, the fire is gradually raised, and maintained for half an hour at a temperature sufficient to melt cast iron. On breaking the crucible after it has cooled, the calcic disilicide is found in the form of a well-fused button, which must be preserved in well-closed vessels.

Calcic disilicide has a leaden-grey metallic lustre and a scaly crystalline structure, with an indistinct indication of hexagonal plates. When exposed to the air, it crumbles down slowly into a mass of graphite-like plates. If thrown into water a similar change occurs, attended with a very gradual but prolonged disengagement of hydrogen. This disintegration is due to the hydration and oxidation of part of the calcium and silicon, the new products remaining mixed with some unaltered silicide. Fuming nitric acid does not attack the calcic disilicide. Hydrochloric acid, as well as dilute sulphuric and acetic acids, convert it into the yellow substance already described (493), whilst hydrogen escapes.

Calcic disilicide has, in the hands of Wöhler, proved a source from which he has been enabled to procure various compounds of silicon, hydrogen, and oxygen, presenting some analogy with the compounds of carbon with the same elements, and will probably give rise to further researches of importance.

(717) **CALCIC SULPHATE,** or *Sulphate of calcium;* $CaSO_4 = 136$; *Density,* 2·95; *Comp. in* 100 *parts,* CaO, 41·18; SO_3, 58·82; *crystallized as gypsum;* $CaSO_4.2OH_2 = 172$; *Density,* 2·30; *water in* 100 *parts,* 20·93.—The mineral *anhydrite* which is found in the salt rocks of the Tyrol, and in Upper Austria, crystallizes in rectangular prisms, and consists of anhydrous calcic sulphate; the sulphate however is much more abundant as a hydrate with $2OH_2$: it is then met with either in transparent flattened prisms, known as *selenite,* or still more frequently in a fibrous, granular, compact, or earthy form, constituting the different varieties of *gypsum* and *alabaster.* Calcic sulphate is a very common impurity in spring water. Water saturated at 0° (32° F.) contains one part of $CaSO_4$ to 525 of water, and the

solubility increases up to 38° (100°·4 F.) when 1 part requires 466 of water to dissolve it: as the temperature rises, however, the solubility of the salt again diminishes: at 18° (64°·4 F.) a litre of water dissolves 2·1 grams; but, according to Chandler, at a temperature of 124° (255°·2 F.), when the pressure is equal to that of about two atmospheres of steam, little more than one-fourth of this amount is held in solution; whilst under a pressure of three atmospheres, or at 133° (271°·4 F.), not more than one-twentieth is soluble, and at a temperature of 150° (302° F.) it is practically insoluble. The presence of chlorides of calcium and magnesium diminish the solubility of calcic sulphate, whilst sodic thiosulphate (hyposulphite) is said to increase it tenfold. Waters which contain calcic sulphate in solution are often termed *selenitic*; they deposit upon the interior of boilers in which they are used, a strongly adherent fur or crust, the composition of which is $2CaSO_4.OH_2$.

Calcic sulphate is produced whenever a strong solution of a calcium salt is precipitated by any sulphate, in which case it falls as a white voluminous sparingly soluble hydrate. It is insoluble in alcohol, but it is dissolved to some extent by dilute nitric and hydrochloric acids. When heated, it loses its water, and if the temperature be raised to bright redness, the anhydrous mass fuses, and may be obtained in crystals of the same form as those of anhydrite.

Gypsum constitutes a manure of considerable utility when judiciously employed; but the most remarkable property of calcic sulphate, and that for which it is chiefly valued, is the power which the hydrated variety possesses, after it has been deprived of water by a heat not exceeding 260° (500° F.), of again combining with water, and binding or setting into a hard mass. The friable mass obtained by depriving gypsum of water and reducing it to a fine powder constitutes what is known as *plaster of Paris*, from the circumstance that it is largely manufactured in the vicinity of the French metropolis. If the dry powder be made into a thin paste with water, the mixture becomes solid in a few minutes, expands perceptibly at the moment of solidification, and experiences a considerable rise of temperature, which in large masses may amount to 25° or 30° (45° or 54° F.): a combination of 2 molecules of water with 1 molecule of calcic sulphate occurs, and eventually it becomes as hard as the original gypsum, each molecule of the salt recombining with the 2 molecules of water it had lost. It is, however, particularly worthy of observation, that if the sulphate be heated to redness, it becomes very much

denser, assumes a crystalline structure, and loses the power of setting or solidifying when mixed with water.

Plaster of Paris is manufactured in large quantities for architectural purposes: it is also extensively used in modelling, and taking accurate copies of objects of every description. Suppose, for instance, it were desired to copy a medal: a raised rim of pasteboard is attached to the medal, which is anointed with a little oil, to prevent the plaster from adhering to its surface. The dried plaster is then mixed with water until it is of the consistence of thin cream, and is immediately applied carefully with a hair pencil to every part of the surface, so as to exclude air; after which a thicker cream is poured into the mould: in a few minutes the mass becomes solid, and the cast may be removed from the medal.

The addition of 1 or 2 per cent. of many salts—particularly of alum, of potassic sulphate, or of borax—confers upon gypsum some properties of considerable practical importance. Gypsum which has been thus treated will endure a dull red heat without losing its power of setting when mixed with water. It becomes much denser than ordinary plaster, and, when mixed with water, sets in the course of a few hours, and forms a hard material which takes a high polish. Keene's, Martin's, and Keating's cement are the respective names under which plaster so treated is known. *Stucco* consists of coloured plaster, mixed with a solution of size. The different colours exhibited by stucco are obtained by the admixture of oxides of iron and other metals. By friction its surface is susceptible of a high polish.

Polyhallite is the mineralogical name for the sulphate of potassium magnesium and calcium, $K_2Ca_2Mg4SO_4.2OH_2$, which is sometimes found native associated with rock-salt, as at Stassfurth, and has been formed occasionally during the manufacture of tartaric acid. It is decomposed by water.

Calcic sulphate also forms a double salt with sodic sulphate, which occurs native under the name of *glauberite* or *brongniartin*, Na_2Ca2SO_4; it is anhydrous, and nearly insoluble in water. Other double sulphates have been obtained artificially as *potassic calcic sulphate*, $K_2Ca2SO_4.OH_2$, and *ammonic calcic sulphate*, $(NH_4)_2Ca2SO_4.OH_2$.

(718) **CALCIC NITRATE**, or *Nitrate of calcium*; $Ca2NO_3.4OH_2 = 164+72$: *Density, anhydrous*, 2·24; *cryst.* 1·780.—This is a deliquescent salt, which crystallizes in long prisms: when anhydrous, it emits light if gently heated. It is soluble in alcohol.

(719) **CALCIC CARBONATE**, or *Carbonate of lime*; $CaCO_3 = 100$: *Density of Iceland spar*, 2·72; *of Aragonite*, 2·97; *Comp. in* 100 *parts*, CaO, 56; CO_2, 44.—This substance is one of the most abundant components of rocks and minerals. In the uncrystallized condition it forms the different varieties of *limestone, oölite, chalk*, and *calcareous marl*; it is the principal constituent of corals, of the shells of mollusca, and of the eggshells of birds; it also enters in greater or less quantity into the bones of animals. In minute granular crystals it forms the different kinds of *marble*, and it is found in a greater variety of regular

crystalline forms than any other compound. Its primary form is a rhombohedron, as is seen in *Iceland spar*, but it also occurs in the incompatible form of *aragonite*, in six-sided prisms, and is consequently dimorphous. Aragonite is isomorphous with strontic carbonate, and its crystals not unfrequently contain small quantities of this mineral, the occurrence of which it is supposed may assist in determining the assumption of the prismatic form by the calcic carbonate. When aragonite is heated it falls to powder, and the grains are stated to assume the form of minute rhombs. Calcic carbonate is produced whenever a calcium salt is precipitated by the addition of an alkaline carbonate, and if the solutions be mixed at the boiling-point, the carbonate falls in microscopic crystals having the form of aragonite. Credner (*Jahrbuch f. Mineralogie*, 1871, 188) has made an interesting series of experiments on the conditions under which calcic carbonate separates from solutions of the bicarbonate in the two crystalline forms.

It is sometimes necessary to obtain a perfectly pure calcic carbonate; for this purpose a solution of calcic nitrate may be mixed with an excess of lime-water, which precipitates magnesia, alumina, ferric oxide, and other metallic oxides; the filtered solution is decomposed by the addition of a mixture of ammonia and ammonic sesquicarbonate, and the precipitate after being washed thoroughly, is dried, and heated to low redness.

Calcic carbonate is decomposed by a red heat, if the gas can freely escape; but according to Sir J. Hall, in closed vessels it fuses without undergoing decomposition, and on cooling becomes converted into a granular crystalline mass, like marble.

A combination of calcic and sodic carbonates, insoluble in water, was found at Merida, in South America, and called *Gay-Lussite*, $CaNa_2 2CO_3 . 5OH_2$. *Barytocalcite*, $CaBa2CO_3$, is a native double carbonate of calcium and barium, which crystallizes in oblique prisms.

(720) **Calcareous Waters.**—Calcic carbonate is soluble in pure water to the extent of about 0·3 mgrm. per litre, or rather more than 2 grains in 1 gallon, but it is freely taken up by water containing carbonic acid, and is deposited again in anhydrous crystals as the gas escapes. In this way enormous masses of crystallized calcic carbonate are formed. In the limestone hills of Derbyshire, and in various other localities, caverns occur in which this phenomenon is perpetually exhibited; water containing carbonic acid and calcic carbonate makes its way through the roof of the cavern, where, as the carbonic anhydride gradually

escapes, the carbonate is deposited in dependent masses, like icicles, termed *stalactites;* whilst the water, falling on the floor of the cavern before it has parted with all its excess of carbonic acid and dissolved limestone, deposits a fresh portion of the crystalline matter; and thus a new growth, or *stalagmite*, gradually rises up to meet the stalactite which depends from the roof: in this way a natural pillar of crystallized calcic carbonate is formed.

It is in a similar manner that the calcareous deposits from the lakes of volcanic districts are produced. These deposits, when porous, have received the name of *tufa;* when more compact, they are termed *travertine.* Travertine is formed abundantly in many of the Italian lakes; it was highly valued for architectural purposes by the Romans, as it is a material easily wrought, may be polished readily, and possesses great durability and beauty.

Many spring waters contain calcic carbonate held in solution by carbonic acid, and when the water is boiled, carbonic anhydride is expelled; the carbonate is then deposited, forming a more or less coherent lining upon the sides of the vessel. In steam boilers this becomes a serious evil, but it may be effectually prevented by the addition of a small quantity of soda-ash or of sal ammoniac to the water; in the latter case ammonic carbonate is formed, and volatilized, whilst calcic chloride remains dissolved.

Dr. T. Clark contrived a plan for softening such calcareous waters, by removing the carbonic acid from them, and thus causing the precipitation of the calcic carbonate by depriving it of its solvent (p. 62). This method consists essentially in the addition of milk of lime to such waters, until the water gives a very faint brown tinge on testing it with a solution of argentic nitrate: this reaction indicates that a slight excess of lime has been added, which occasions a precipitate of brown hydrated argentic oxide. In this operation the lime combines with the excess of carbonic acid in the water: the calcic carbonate thus formed, being insoluble, is precipitated along with the portion of calcic carbonate previously held in solution by the carbonic acid. After the lapse of twenty-four hours the water becomes perfectly bright and clear. If colouring or organic matters be present in the water, a considerable portion of both goes down with the chalk. In applying this process upon a large scale, it is found advantageous to add a slight excess of lime in the first instance,

and afterwards to destroy this excess by a fresh addition of unlimed water. The carbonate is then separated in granular crystals, which speedily subside; these crystals are formed much more slowly if the lime be not at first in slight excess. Where the water contains calcic sulphate in quantity, baric chloride may be employed in conjunction with Clark's process, taking care not to add excess of the baric salt: in this case the sparingly soluble calcic sulphate is replaced by the exceedingly soluble chloride, which is of considerable advantage when the water is required to feed steam boilers.

(721) **Clark's Soap-test.**—Dr. Clark has introduced a method of testing the hardness of waters by the application of the *Soap-test*, which has been extensively used. The operation may be conducted in the following manner:

A solution of soap in proof spirit (containing about 120 grains of curd soap to the gallon) is first prepared. In order to graduate this solution, 16 grains of Iceland spar, or Carrara marble, are dissolved in a flask in pure hydrochloric acid, evaporated to dryness in the flask, redissolved in water, and a second time evaporated to dryness. On again dissolving it in water, a perfectly neutral solution of calcic chloride is obtained; this solution is then diluted with distilled water until it measures 1 gallon. It will now represent a water of 16° of hardness; that is to say, it will correspond in hardness to a water containing 16 grains of calcic carbonate per gallon, each degree of hardness upon Clark's scale representing an amount of any calcium salt corresponding to 1 grain of chalk per gallon in the water. 1000 water-grain measures of this solution are next transferred by a pipette, graduated to deliver exactly this quantity, into a well-stoppered bottle which will hold 5 ounces. The soap solution is then added to the water from a burette, each division of which corresponds to 10 water-grains. After each addition of the soap-test, the stopper is replaced in the bottle, which is shaken briskly for a minute, and then laid upon its side; fresh portions of the soap being added in small quantities until a fine lather in uniform small bubbles remains unbroken over the surface for three minutes. The number of measures of the soap-test employed is noted, and the strength of the solution is increased or diminished by the addition of soap or of spirit, as may be necessary, until exactly 32 measures are required for 1000 water-grains of the standard solution of 16° of hardness. After the solution has been made up to this strength, the experiment is repeated, in order to ascertain that the adjustment is correct.

In applying the test, 1000 measured grains of the water to be examined are introduced into the stoppered bottle, and the operation is proceeded with as above, reading off the number of test-measures required, in order to produce a permanent lather. The degree of hardness of the water is then obtained by simple inspection of the subjoined table, The results are, however, apt to be inaccurate, if large quantities of magnesium salts are present (D. Campbell, *Phil. Mag.*, 1850, xxxvii. 171). Sometimes the water exceeds 16° in hardness; in that case it should be diluted with an equal measure, or, if necessary, with twice, or even with thrice its bulk of distilled water. 1000 grain-measures of the diluted water are then to be tested as usual, and the number of divisions of the soap-test employed is to be read off, and the degree of hardness corresponding to it is noted from the table. This degree must be finally multiplied by 2, by 3, or by 4, according to the extent to which the water had been previously diluted.

Clark's Table of Hardness of Water.

Degree of hardness.	Measures of soap-test.	Diff. for the next 1° of hardness.
0 (Distilled water)	1·4	
1	3·2	1·8
2	5·4	2·2
3	7·6	2·2
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	2·0
8	17·5	1·9
9	19·4	1·9
10	21·3	1·9
11	23·1	1·8
12	24 9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·8
16	32·0	1·7

(722) **Building Materials.**—Calcic carbonate forms the basis of some of the materials most highly prized for building purposes, besides furnishing the costly varieties of marble used for interiors. The oölites, such as those from the Isle of Portland and the neighbourhood of Bath, resist the weather admirably; they admit of being readily fitted and cut, and yet possess considerable hardness. Many shelly limestones are also well adapted for these purposes. Where elaborate carving is required, a well-crystallized magnesian limestone (or double carbonate of calcium and magnesium), such as that employed in the Houses of Parliament, is preferred; it is very close and compact, sufficiently soft to be easily sculptured, but retains a sharp outline.

Many fine-grained, porous, calcareous and magnesian stones have the inconvenience of splitting into flakes after a few years' exposure; this generally occurs from the absorption of water, and its expansion when the moisture thus absorbed becomes frozen during winter. A simple and ingenious mode of ascertaining whether a building-stone is liable to this defect was invented by Brard:—It consists in taking a smoothly-cut block of the stone, 3 or 5 centim. or one or two inches in the side, and placing it in a cold saturated solution of sodic sulphate. The solution is gradually raised to the boiling-point, and maintained at that temperature for half an hour, the stone being left to cool in the liquid. When cold, it is suspended over a dish, and once a day for a week or a fortnight plunged for a few moments into a cold saturated solution of sodic sulphate, and is then again freely suspended in the air. The sulphate crystallizes in the pores of the stone, and splits fragments off from it. A similar experiment is made upon an equal sized mass of stone which is known to be free from this defect. By the comparative weight of these fragments in the two cases the tendency of the stone to the defect in question may be estimated.

A stone which is placed in a building conformably to its position in the quarry, so that its seams shall lie horizontally, is much less liable to injury from the weather than where this point is neglected.

In the selection of a building-stone, regard must be had not merely to its durability, but also to the locality in which it is to be placed. A stone which, like a magnesian limestone, may endure unchanged for ages in the open country air, may yet in the atmosphere of a large city become rapidly disintegrated, owing to the action of the sulphuric acid produced by the immense quantities of coal which are burned. Decay from this cause is strikingly shown in the stone used in London in some parts of the Houses of Parliament, and still more so in the new buildings in Lincoln's Inn.

A valuable report upon the composition and quality of various kinds of building stones was made to the British Government in 1839, upon the occasion of the rebuilding of the Houses of Parliament.

The other varieties of building stones are mostly siliceous. To this class belong all the sandstones, which consist chiefly of grains of silica united by a cement more or less ferruginous. The durability of the stone depends mainly upon the character of this uniting material. Many igneous rocks, such as porphyry, basalt, and more especially granite, are also used, but from their hardness they are seldom wrought, except when, as in quays, bridges, or causeways, the constant wear is unusually great, and where softer though less expensive materials would soon be destroyed: they are, however, generally used for building purposes in the immediate neighbourhood of the quarries.

(723) **CALCIC PHOSPHATES.**—Of these, the *tricalcic phosphate*, $Ca_3P_2O_8$, occurs nearly pure in the mineral *osteolite*, and may be prepared artificially by precipitating with calcic chloride a solution of hydric disodic phosphate to which an equivalent of ammonia has been added; when boiled with distilled water, it loses a portion of its phosphoric acid and ultimately leaves a compound having the composition $3Ca_3P_2O_8.CaH_2O_2$ (Warington). Tricalcic phosphate is the principal ingredient of bone-ash, in which it occurs mixed with about one-fourth its weight of magnesic phosphate and calcic carbonate. The compound, Ca_4H3PO_4, formerly supposed by Berzelius to exist in bone-earth, is obtained when an acid solution of tricalcic phosphate is precipitated with ammonia not in excess. This phosphate is insoluble in water, but is readily dissolved by acetic acid and also by the stronger acids. It occurs native as a white amorphous mineral, known under the name of *phosphorite*. Tricalcic phosphate is readily soluble in a solution of sulphurous acid, and the solution when boiled deposits a crystalline precipi-

tate of *tricalcic phosphato-sulphite*, $Ca_3P_2O_8.SO_2.2OH_2$ (Gerland, *Jour. pr. Chem.*, 1871, [2], iv. 97). In the Norfolk crag, considerable deposits of brown rounded pebbles occur, known under the name of *coprolites*, from the supposition that they were the fossilized dung (κόπρος) of extinct animals: they contain a large proportion of calcic phosphate mixed with calcic carbonate and fluoride. Nodules chiefly composed of calcic phosphate are also found abundantly in the green-sand formation near Farnham, and in other localities.

A tricalcic diphosphate occurs naturally crystallized in hexagonal prisms, which, when colourless, are called *apatite*; when of a green colour it is termed *moroxite*; in these minerals three molecules of the phosphate are associated with one molecule of calcic chloride and fluoride: $3Ca_32PO_4.Ca(ClF)_2$. If bone-ash be fused with about 4 times its weight of sodic chloride, and allowed to cool very slowly, delicate crystals having the form of apatite are found lining the cavities contained in the mass (Forchhammer). When hydric disodic phosphate in solution is added drop by drop to an excess of calcic chloride, a semi-crystalline precipitate falls, which consists of dicalcic phosphate, $Ca''HPO_4.2OH_2$, the liquid becoming acid. If the liquid be heated and sufficient acetic acid be added to redissolve the precipitate, the dicalcic phosphate separates in quadratic prisms as the liquid cools.

Several other calcic phosphates may be formed, corresponding in composition to the various sodic phosphates. The soluble acid phosphate, or *superphosphate of lime*, $Ca''H_42PO_4$, is prepared by treating bone-earth with two-thirds of its weight of oil of vitriol, as in the preliminary stage of the extraction of phosphorus. It is largely manufactured as a manure for turnips. If the quantity of sulphuric acid used is insufficient, the insoluble phosphate, $CaHPO_4$, is formed, the reaction taking place in two stages: in the first,

$$Ca_32PO_4 + 2H_2SO_4 = CaH_42PO_4 + 2CaSO_4;$$

the acid 'superphosphate' then reacts with the excess of tricalcic phosphate thus:

$$CaH_42PO_4 + Ca_32PO_4 = 4CaHPO_4.$$

According to Erlenmeyer (*Deut. chem. Ges. Ber.*, 1876, ix. 1839), the acid 'superphosphate,' CaH_42PO_4, although soluble in a large quantity of water is partly decomposed when treated with a comparatively small quantity of water into dicalcic phosphate, $CaHPO_4$, and free phosphorous acid.

(724) **BORO-NATRO-CALCITE.**—A double *Borate of calcium and sodium*, $2(NaCa''3BO_2)3B_2O_3.18OH_2$, is found at Iquique, in Peru, in the form of rounded nodules, composed of fine silky needles. It is but sparingly soluble in hot water, to which it communicates an alkaline reaction; but it is easily dissolved by dilute acids. This mineral has recently been imported into this country to some extent for the preparation of borax, which is easily obtained from it by dissolving the compound in hot dilute hydrochloric acid, and precipitating the calcium as carbonate by the addition of sodic carbonate; the clear, supernatant liquid yields crystals of borax on evaporation, whilst sodic chloride remains in solution. It may also be decomposed by caustic soda (p. 456).

(725) **Characters of the Calcium Salts.**—The calcium salts are colourless. They give no precipitate with *ammonia*, but yield a white precipitate of calcic carbonate, with *ammonic carbonate* and the *carbonates of the alkali-metals*. Solution of *calcic sulphate* produces no precipitate; the calcium salts are thus distinguished from those of barium and strontium: they yield no precipitate with *ammonic hydric sulphide*. *Ammonic oxalate*, even in very dilute neutral or alkaline solutions of salts of calcium, throws down a white calcic oxalate, which is soluble in nitric and hydrochloric acids, but not in acetic acid. Calcic salts give a reddish orange-tinge to flame, and when examined by the spectroscope may be recognized by a bright line in the orange, and a broad rather less luminous band in the green; fainter lines are also visible in the red; and occasionally a bright blue band is seen.

Estimation of Calcium.—In the determination of calcium for analytical purposes the oxalate is the precipitate usually employed; but before weighing, it is heated to dull redness, so as to convert the calcic oxalate into carbonate: 100 parts of the carbonate represent 56 of lime: if heated for a few minutes to a bright red, quicklime is obtained. If no other base is present, calcium may also be estimated in the form of sulphate. If the calcium be not already in the state of sulphate, the salt is heated with an excess of sulphuric acid, and ignited; when cold, it is weighed; 100 grains of calcic sulphate represent 41·18 of lime.

Magnesium will be described in the group containing zinc and cadmium (750 *et seq.*).

CHAPTER XIX.

GROUP III.

METALS OF THE EARTHS.

§ I. ALUMINIUM: Al‴ = 27·5.

(726) **ALUMINIUM**; *Density, from* 2·56 to 2·67. *Fusing-point about* 700° (1292° F.). *Sp. Heat,* 0·2143. *Electric Conductivity* at 20° (68° F.), 33·76. *Atomic Vol. solid,* 10·5. *Triad or more probably Tetrad and capable of existing only in a pseudo-triad condition, as in* $\left\{\begin{matrix}Al'''Cl_3\\Al'''Cl_3\end{matrix}\right.$.—The pure earths are white, insipid, insoluble compounds, the oxides of metals which possess a high attraction for oxygen. A single oxide only of each metal of this class is known.

Of these metals the most abundant and important is ALUMINIUM, which derives its name from one of its compounds, namely, '*alum.*' Indeed, alumina (the oxide of aluminium) constitutes about 10 per cent. of this salt.

Preparation.—1. Aluminium was originally procured by Wöhler, by decomposing aluminic chloride in a porcelain or platinum tube by means of potassium. He obtained it first as a steel-grey powder, and subsequently in malleable globules. In the pulverulent form it is gradually oxidized by boiling water, and more rapidly by alkaline solutions. When heated in this form in oxygen gas, it takes fire and burns with a vivid light, emitting so intense a heat as to fuse the alumina, which forms a yellowish mass, in colour and hardness resembling corundum, a native crystallized alumina.

2.—Bunsen obtains aluminium by the electrolytic decomposition of the double chloride of sodium and aluminium, $2NaCl.Al_2Cl_6$. This salt melts at about 200° (392° F.), and readily furnishes aluminium by a process similar to that adopted in the case of magnesium (750): but as the aluminium is heavier than the fused salt, it is more easily collected than magnesium.

3.—Aluminium may be prepared in the laboratory, by the method of Deville (*Ann. Chim. Phys.*, 1855, [3], xliii. 5).—Into a wide tube of hard glass of an inch or an inch and a half (from 25 to 40$^{mm.}$) in diameter, about half a pound (250 grams) of dry aluminic chloride is introduced, and kept in its place by plugs of asbestos; a current of dry hydrogen, perfectly free from air, is passed over it, and the chloride is very gently heated; in this way traces of hydrochloric acid and chlorides of sulphur and silicon are expelled. Three or four small porcelain trays, each containing 40 or 50 grains (about 3 grams) of sodium, freed from adhering naphtha by pressure between folds of blotting-paper, are then introduced into the tube; the current of hydrogen is still maintained, and heat is applied to the part of the tube which contains the sodium. This end of the tube must be slightly elevated, in order to prevent the melted aluminic chloride from running down upon the sodium; in which case the heat emitted is so intense as to crack the tube. When the sodium is melted, the aluminic chloride

is gradually distilled over by the application of a regulated heat, and is reduced with vivid incandescence. The aluminium is condensed in the porcelain trays, in which also a sodic aluminic chloride collects around the reduced aluminium. These trays and their contents when cold are withdrawn from the glass tube, and placed in a porcelain tube, through which a current of hydrogen is passed, whilst the tube is raised to a bright red heat; the aluminium fuses into globules in the porcelain trays; and by fusing it once more in a porcelain crucible under a layer of the sodic aluminic chloride, a button of pure aluminium is obtained.

Messrs. Bell of Newcastle have carried out the process of Deville as a manufacturing operation. They prepare a trisodic aluminate, $3Na_2O.Al_2O_3$, from Bauxite, an aluminous ore of iron nearly free from silica (732), and precipitate the alumina as hydrate, by means of carbonic or hydrochloric acid. The precipitated aluminic hydrate is then mixed with common salt and charcoal, made into balls of the size of an orange, and dried. These balls are placed in vertical earthen retorts heated to redness, and through them dried chlorine is transmitted. The sodic aluminic chloride, $2NaCl.Al_2Cl_6$, distils over. Ten parts of this double salt and 5 of cryolite or fluor-spar are thrown with 2 parts of sodium into a reverberatory furnace, previously raised to the proper temperature, and the damper is then closed. An intense reaction, attended with great evolution of heat, occurs, the chlorine combines with the sodium, and the metallic aluminium collects at the bottom in a melted form.

4.—Rose prepares aluminium from cryolite, $6NaF.Al_2F_6$, by fusing it with sodium. For this purpose Wöhler recommends 7 parts of sodic chloride to be melted with 9 of potassic chloride, and the mass thus obtained to be finely powdered and intimately mixed with its own weight of cryolite in fine powder. This powder is to be introduced with a fifth or sixth of its weight of sodium (arranged in alternate layers of the powder and the metal), into a dry earthen crucible, which is to be heated rapidly in a wind furnace. An intense reaction occurs, and a portion of the sodium burns off. The mixture is afterwards heated for about a quarter of an hour until it is entirely fused, and is then allowed to cool. The aluminium collects at the bottom in a well-formed button, which is frequently crystalline on its surface. In some experiments the quantity of reduced metal amounted to one-third of that present in the mineral employed.

5.—It has also been proposed (Bassett) to prepare an alloy of aluminium and zinc by treating the double aluminic sodic chloride with zinc, and then to remove the excess of the latter by distillation, but probably owing to the high temperature required for this purpose it has not superseded the sodium processes.

(727) **Properties of Aluminium.**—As prepared by Deville's process, aluminium is a white malleable metal, nearly resembling zinc in colour and hardness: it may be rolled or beaten into very thin foil, and admits of being drawn into fine wire; after it has been rolled, it becomes much harder and more elastic. It conducts electricity with about one-third the power of silver. Aluminium is remarkably sonorous, and emits a clear musical sound when struck with a hard body. Fused aluminium crystallizes readily as it cools, apparently in regular octohedra; its point of fusion is below that of silver: when melted it may easily be cast in moulds of metal or of sand. It can be heated intensely in a current of air in a muffle without undergoing more than a superficial oxidation, and it is but slowly oxidized when heated to full redness in an atmosphere of steam. When in the form of foil it may be ignited in oxygen by an incandescent splinter of charcoal, when it burns with a brilliant bluish-white light. Aluminium shows no tendency to volatilize, either when heated intensely in closed vessels or when subjected to a succession of electric sparks.

Aluminium alone does not decompose water at the ordinary temperature, but it does so readily in presence of aluminic iodide, with evolution of hydrogen, the reaction being: $Al_2I_6 + 3OH_2 = Al_2O_3 + 6HI$ and $6HI + Al_2 = Al_2I_6 + 3H_2$ (Gladstone and Tribe). Nitric acid, whether concentrated or dilute, is without action upon aluminium at the ordinary temperature, and dissolves it very slowly even when boiling. Both concentrated and dilute hydrochloric acid, on the contrary, attack it rapidly, forming aluminic chloride, whilst hydrogen is disengaged. Solutions of the alkalies, especially when aided by heat, also attack aluminium with energy, producing alumina, which is dissolved by the alkaline solution, whilst hydrogen gas is liberated. From its lightness and inalterability in the air, aluminium has been applied to the preparation of small weights: the metal is chiefly used, however, for ornamental articles, and for some philosophical instruments where lightness and rigidity are required, but some difficulty was at first experienced in working the metal for want of a suitable solder. The solder now generally preferred is an alloy of 4 parts of copper, 6 of aluminium, and 90 of zinc. No flux is used, and it is proposed to employ small soldering tools of aluminium.

Aluminium readily forms alloys with copper, silver, and iron, but it may be melted with lead without any combination between the two metals taking place. Its alloys with copper are very

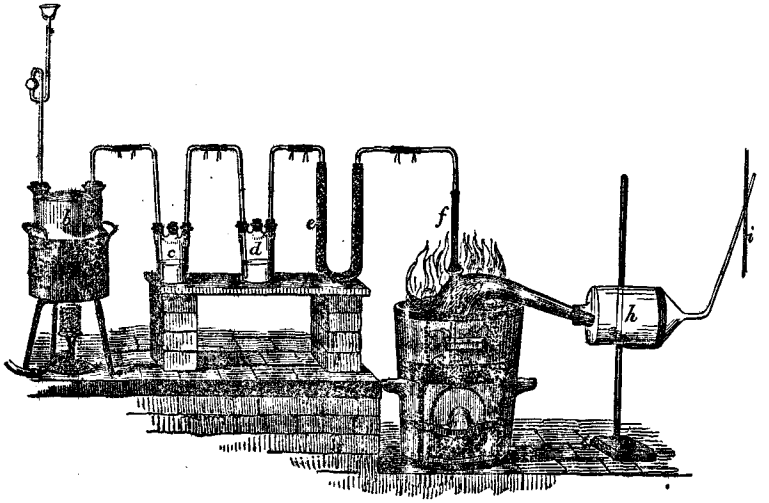
hard, and susceptible of a high polish; they vary in colour from white to golden yellow, according to the proportion of the two metals: one of these, Cu_9Al, a beautiful alloy of a golden yellow colour, containing about 10 per cent. of aluminium, is manufactured by Messrs. Bell under the name of *aluminium bronze*: it is well fitted for castings, and possesses great tenacity and hardness. For the preparation of this alloy, copper of great purity is needed. Aluminium also combines readily with carbon and silicon, forming greyish, granular, brittle, crystalline compounds, which present a considerable analogy to cast iron. From solutions of the nitrate, chloride, and cyanide of mercury, aluminium throws down metallic mercury, which forms an amalgam with the excess of aluminium. This amalgam decomposes water at the ordinary temperature, and when exposed to the air oxidizes with great rise of temperature: this accounts for the fact that when a plate of aluminium is rubbed over with a piece of leather impregnated with mercury, or with moistened mercuric chloride, iodide, or oxide, or mercurous chloride, a powerful action takes place accompanied by the production of a white exfoliated crust of alumina.

Finely divided aluminium burns brilliantly in the vapour of sulphur, forming a black sesquisulphide, Al_2S_3, of semi-metallic appearance; this is rapidly decomposed by water, with formation of hydrated alumina and sulphuretted hydrogen.

(728) **ALUMINIC CHLORIDE,** or *Chloride of aluminium*; $Al_2Cl_6=268$, $\left[\begin{Bmatrix}Al'''Cl_3\\Al'''Cl_3\end{Bmatrix}\right]$; *Theoretic Density of Vapour*, 9·27; *Observed*, 9·32; *Mol. Vol.* [ ]; *Rel. wt.* 134.—The anhydrous chloride cannot be formed directly by dissolving alumina in hydrochloric acid and evaporating to dryness, since during the expulsion of the water, a great part of the acid is also driven off. It may be procured as a yellow, anhydrous, volatile sublimate, by a process devised by Oersted: alumina, mixed with charcoal powder, is made up into paste with starch or oil, and subdivided into pellets: these pellets are charred in a covered crucible, and then exposed to ignition in a current of dry chlorine. In this operation, carbon, in a very finely divided state, is mixed with the alumina; when the mass is heated with chlorine, the carbon unites with the oxygen of the alumina, and the chlorine seizes the liberated aluminium; $Al_2O_3+3C+3Cl_2=Al_2Cl_6+3CO$. Aluminic chloride condenses in the cool part of the tube in a crystalline, somewhat translucent mass, or as an amorphous powder.

In preparing this chloride in the laboratory, an apparatus similar to that shown in fig. 348 may be used: *b* is a vessel containing a mixture of black oxide of manganese and hydrochloric acid, for generating chlorine: *a* is a water-jacket, for applying a moderate heat; *c* is a wash-bottle containing water; *d* contains strong sulphuric acid; *e* is a bent tube filled with pumice-stone saturated with oil of vitriol, to remove the last traces of moisture; *g* is an earthen retort filled with the mixture of charcoal and alumina, heated by a charcoal fire.

FIG. 348.



The chlorine is conveyed nearly to the bottom of this retort by means of a porcelain tube, *f*, luted into the tubulure: the gas reacts upon the mixture in the retort, forming carbonic oxide and aluminic chloride, the latter of which condenses in the gas-jar, *h*, provided for its reception: the open mouth of this jar is closed by means of a funnel, luted on with a strip of pasted paper; and the carbonic oxide escapes through the open tube, *i*, into the chimney. In order to purify crude aluminic chloride from the small quantity of volatile ferric chloride which usually accompanies it, the compound is redistilled from iron wire, by which the ferric chloride is converted into the much less volatile ferrous chloride, and the aluminic chloride sublimes nearly in a state of purity.

Deville prepares this chloride on a large scale from a mixture of coal tar and alumina, which is heated first in iron pots until the vapours of tar cease to escape, and then in a clay retort, such as is used in gas making, but set vertically; a current of chlorine is sent over the ignited mass, and the product of the operation is received in a chamber lined with glazed brickwork. (Compare 726, 3.)

Aluminic chloride is also formed together with sulphur and sulphuretted hydrogen on passing dry hydrochloric acid mixed with carbonic bisulphide vapour over alumina heated to redness. It is purified by distilling it from iron filings, which retain the sulphur and ferric chloride. If clay be used, silicic chloride is also formed, but being very volatile it passes off in the state of vapour.

If aluminic chloride be heated in considerable mass, it melts

at a dull red heat, and near its fusing-point sublimes rapidly; when exposed to the air it emits fumes of hydrochloric acid: it is soluble in alcohol, is very deliquescent, and when thrown into water hisses from the heat developed by the violence of the combination. The aqueous solution, when concentrated by a very moderate heat, yields six-sided prisms of the hydrate $Al_2Cl_6.12OH_2$. By subliming the anhydrous chloride in a current of sulphuretted hydrogen, it forms a compound with this gas, which is decomposed by resublimation, or by solution in water. The chloride may also be made to combine with phosphuretted hydrogen, and with ammonia.

(729) **Aluminic Bromide**, $Al_2Br_6=535$; *Mol. Vol.* [ ]; *Rel. wt.* 267·5; *Theoretic Density of Vapour*, 18·51; *Observed*, 18·6: *and* **Aluminic Iodide**, $Al_2I_6=817$; *Mol. Vol.* [ ]; *Rel. wt.* 408·5; *Theoretic Density of Vapour*, 28·268; *Observed*, 28·227, have also been obtained.

(730) **ALUMINIC FLUORIDE** occurs native, combined with sodic fluoride, as *cryolite*, $6NaF.Al_2F_6$. It is found in large quantity in Greenland, and as it is easily decomposed by sodium, it has been proposed as a source of metallic aluminium, of which it contains 13 per cent. Another highly prized aluminous mineral, containing fluorine, is the *topaz*. It is extremely hard; the colourless variety has a lustre which has sometimes caused it to be mistaken for the diamond. Its composition may be represented by the formula

$$2(Al_2O_3.SiO_2).Al_2O_3.SiF.$$

(731) **ALUMINA**, or *Aluminic oxide*; $Al_2O_3=103$; *Density of ruby*, 3·95; *Comp. in* 100 *parts*, Al, 53·39; O, 46·61.—This is the only known oxide of aluminium: from its isomorphism with the sesquioxide of iron, and its general resemblance to it in properties, and also from the vapour density of aluminic chloride,* it is regarded as a sesquioxide. It forms one of the materials that enter most largely into the composition of the superficial strata of the earth. It is the basis of all the varieties of clay, and is present in greater or less quantity in almost every soil. Alumina occurs nearly pure, and crystallized in six-sided prisms, in *corundum*, in which mineral it has a density of 3·95, and is hard enough to cut glass. The *sapphire* and the *ruby* are also composed of this earth, tinged with a small quantity of oxide of chromium. They are only inferior to the diamond in hardness. *Emery* is another form of alumina coloured with oxides of iron

* It may be, however, that if the vapour density of aluminic chloride were taken at a temperature very much higher than its boiling-point, it would be found to correspond to the formula $AlCl_3$ instead of Al_2Cl_6, for it seems highly probable that aluminium is a triad.

and manganese, which from its hardness is largely used in grinding and polishing.

Alumina may be obtained by intensely igniting pure ammonia alum, $(NH_4)_2Al'''_2\,4SO_4.24OH_2$, for some time: the water, ammonia, and sulphuric acid are expelled, and anhydrous alumina is left, in the proportion of 11·34 parts of alumina to 100 of the crystallized salt. It is, however, nearly impossible to drive off the last portions of sulphuric acid, as the salt swells up enormously, and forms a white, porous, infusible mass, which is an extremely bad conductor of heat. Alumina may also be prepared by precipitation from alum free from all trace of iron; the salt should be dissolved in water and decomposed by potassic carbonate in slight excess: the liquid should be warmed, and the precipitate well washed; but since traces of potash obstinately adhere to it, it must be redissolved in hydrochloric acid, and again thrown down by ammonia or ammonic carbonate; it then forms a white, semitransparent, bulky, gelatinous hydrate, which must be again thoroughly washed; it is completely soluble in a solution of potassic hydrate, and is readily taken up by acids. On drying, it contracts very much, and forms a yellowish translucent mass, like gum, containing $Al_2H_6O_6$. *Diaspore* is a natural hydrate, $Al_2O_3.OH_2$ or $\begin{cases}AlO(OH)\\AlO(OH)\end{cases}$, which decrepitates strongly when heated and falls to powder. Alumina may also be obtained from trisodic aluminate (732) by adding hydrochloric acid in quantity just sufficient to form sodic chloride.

Aluminic hydrate when ignited loses its water, and at a certain temperature presents an appearance of sudden incandescence; it contracts greatly at the moment when this phenomenon takes place, and is afterwards nearly insoluble in acids. Hydrated alumina is strongly hygroscopic, and when applied to the tongue adheres to it.

Alumina fuses before the oxyhydrogen blowpipe, and yields a colourless transparent mass, resembling corundum. Gaudin states that artificial crystals, having the form and hardness of the ruby, may be obtained by calcining equal parts of potassic sulphate and alum, and introducing the mixture in fine powder into a crucible lined with lampblack. The cover is then to be luted on, and the crucible exposed to the highest heat of a forge for a quarter of an hour. In this operation the sulphuric acid of the aluminic sulphate is expelled, the potassic sulphate is reduced to dipotassic sulphide, and this compound dissolves a portion of the liberated alumina, depositing it again in minute prismatic colourless crys-

tals, during the slow cooling of the mass. These crystals may be freed from adhering impurities by digestion in dilute aqua regia. Similar minute crystals have also been obtained by Deville, who has succeeded in imitating the hue both of the ruby and the sapphire. Alumina forms salts with the more powerful acids, but these salts are readily decomposed: they all have an acid reaction, and indeed alumina possesses properties which approach somewhat to those of an acid, as it has a strong tendency to unite with basic oxides. The *spinelle ruby*, for example, is a native magnesic aluminate, $MgO.Al_2O_3$, and *gahnite* is a zincic aluminate, $ZnO.Al_2O_3$. Fremy has also obtained a white granular oxide of aluminium and potassium, to which he assigns a composition corresponding to the formula, $K_2O.Al_2O_3$; these bodies may be regarded as salts of which diaspore is the corresponding acid $\left[\text{Gahnite}\left\{\begin{matrix}AlO\\AlO\end{matrix}\right.(O_2Zn)''\right]$. When the solution of alumina in potassic or sodic hydrate is exposed to the air, it absorbs carbonic anhydride, and an aluminic trihydrate is deposited in regular crystals.

Alumina when combined with silica forms clay, which is the basis of porcelain and of earthenware. To the dyer and the calico-printer the compounds of alumina are of high value: hydrated alumina has the property of combining intimately with certain kinds of organic matter, and when aluminic salts are mingled with coloured vegetable or animal solutions, and precipitated by the addition of an alkali, the alumina carries down the greater portion of the colouring matter, forming a species of pigment termed a *lake*. By soaking the cloth with a preparation of alumina, the earth attaches itself to the fibre; and if cloth thus prepared be plunged into a bath of the colouring matter, it becomes permanently dyed. Most colouring matters would be removed by washing, were it not for the intervention of some *mordant*, or substance which thus adheres to the fibre as well as to the colouring matter. Stannic oxide, and ferric and chromic oxides, resemble alumina in this respect, and are largely used as mordants in dyeing calicoes and woollens.

Mr. Crum (*Jour. Chem. Soc.*, 1853, vi. 216) has described a remarkable modification of hydrated alumina, which, in the presence of a very small proportion of acetic acid, is largely soluble in water, and is coagulated and rendered insoluble by a minute trace of sulphuric acid. It appears from the experiments of Péan de St. Gilles (*Ann. Chim. Phys.*, 1856, [3], xlvi. 47) that ferric oxide admits of a similar modification: various other soluble colloidal oxides have also been described by Graham (*Phil. Trans.*, 1861, and *Proc. Roy. Soc.*, 1864).

(732) **TRISODIC ALUMINATE**, or *Aluminate of sodium*: $Na_6Al_2O_6$.—This compound now forms an article of commerce, and is obtained from *Bauxite*, a hydrated aluminous ferric oxide, which contains from 60 to 75 per cent. of alumina, and only from 1 to 3 per cent. of silica. This ore is mixed in fine powder with sodic carbonate or soda-ash, and heated to bright redness until no effervescence occurs on the addition of an acid. On lixiviation, the aluminate is dissolved out and separated, by filtration into a vessel, from which, to accelerate the operation, the air is exhausted. The filtrate when evaporated to dryness gives a whitish, infusible, but freely soluble compound, which furnishes a valuable material in the preparation of lakes for pigments, as well as for the purposes of a mordant to the calico-printer, and has in certain instances superseded the use of the different forms of alum. The silica remains behind in the form of an insoluble sodic aluminic silicate.

If a solution of trisodic aluminate is exposed to the action of a current of carbonic anhydride, sodic carbonate is produced, and hydrated alumina precipitated contaminated with soda. If hydrochloric acid in quantity sufficient to neutralize the soda be added to a solution of the aluminate, the alumina is precipitated in a form in which it may be washed: but the precipitate is simply dried when it is to be used in the preparation of aluminium, for which it is chiefly required; the presence of sodic chloride being advantageous in the subsequent operations. A curious reaction occurs when solutions of trisodic aluminate and aluminic chloride are mixed in equivalent proportions; sodic chloride is formed, and the alumina from both compounds is precipitated in the form of hydrate; $Na_6Al_2O_6 + Al_2Cl_6 + 6OH_2 = 2Al_2H_6O_6 + 6NaCl$.

(733) **ALUMINIC SULPHIDE**, $Al_2S_3 = 151$.—This compound is formed by the action of sulphur on aluminium at high temperatures, and also when alumina is heated in the vapour of carbonic bisulphide. It is usually obtained as a yellow coherent powder, which fuses with difficulty, and on cooling forms a hard crystalline mass: exposed to moist air, it disengages sulphuretted hydrogen and leaves alumina:

$$Al_2S_3 + 6OH_2 = Al_2H_6O_6 + 3SH_2.$$

It burns in the air with formation of sulphurous anhydride and alumina.

(734) **ALUMINIC NITRIDE**, Al_2N_2.—This compound is produced when metallic aluminium is mixed with sodic carbonate and strongly heated in a furnace. The aluminium left, when treated with hydrochloric acid, leaves the nitride in crystalline grains (Mallet, *Jour. Chem. Soc.*, 1876, ii. 352).

(735) **ALUMINIC SULPHATE**, or *Sesquisulphate of aluminium*; $Al_23SO_4.18OH_2 = 343 + 324$; *Density*, 1·671.—This salt

occurs native in delicate fibrous masses, and is formed artificially by dissolving alumina in sulphuric acid. It is now manufactured on a large scale in the north of England, by mixing finely-powdered clay or shale, after it has been gently roasted, with about half its weight of crude sulphuric acid from the chambers, and heating it gradually in a reverberatory furnace until fumes of acid begin to escape; this digestion is continued for 3 or 4 days, after which the mass is lixiviated, and the solution thus obtained is freed from iron by the addition of potassic or sodic ferrocyanide so long as it occasions a blue precipitate; the clear liquid is decanted and evaporated, and the residue is sold under the name of *concentrated alum*. It crystallizes in thin flexible nacreous scales, which are soluble in twice their weight of cold water; this solution may be used as a test for potassium, for by mixing it with a solution containing a salt of this metal, and evaporating, octohedral crystals of alum are deposited. Aluminic sulphate has a strong tendency to form double salts with monobasic sulphates, of which those with the sulphates of potassium and ammonium, constituting potash- and ammonia-alum respectively, are the most important. A remarkable anhydrous aluminic sulphate, which assumes the form of a white mealy powder, insoluble in cold water, but which may be rendered soluble, and converted into the ordinary sulphate by prolonged boiling, is obtained by boiling either cryolite, or ordinary alum, with from three to ten times its weight of oil of vitriol, and distilling off about three-fourths of the sulphuric acid; the acid sulphate of potassium or of sodium may be removed by washing, and the anhydrous aluminic sulphate is left as a white powder, analogous to the corresponding modification of the ferric and chromic sulphates (Persoz).

A basic aluminic sulphate, soluble in water, and of a yellow colour, may be obtained; the yellow tint is not due to the presence of ferric sulphate (Siewert).

(736) **ALUM**; *Potassic aluminic sulphate*, $K_2Al_24SO_4.24OH_2$ $=517{\cdot}2+432$; *Density, anhydr.* 2·228; *cryst.* 1·726.—This valuable salt is occasionally found native in volcanic districts, as at Pozzuoli, near Naples, in the form of a white efflorescence, produced by the action of the sulphuric acid of the volcano upon the compounds of aluminium and potassium contained in the lava and trachytic rocks. For the purposes of commerce, however, alum is manufactured artificially. Three principal methods are adopted:

1.—In the first the alum is prepared by the addition of

potassic sulphate or chloride to the crude aluminic sulphate prepared from clay by the process just described.

2.—A still simpler method is practised in Italy, where, especially in the neighbourhood of Civita Vecchia, the *alunite* or *alum-stone* is abundant. This rock contains the elements of alum, with an excess of hydrated alumina, mixed with a variable proportion of siliceous matter. The ore is first roasted at a gentle heat in kilns, avoiding direct contact with the fuel: water is thus expelled, and the mass is rendered spongy; the hydrated alumina parts with its water, and the formation of a basic sulphate of aluminium and potassium, which is insoluble in water, is thereby prevented. The roasted ore is then arranged in long heaps or ridges upon a firm clay floor, where it is frequently moistened with water: in the course of two or three months the mass crumbles down into a sort of mud, which is lixiviated, and the solution when evaporated yields crystals of alum, which after a second crystallization are fit for the market. This variety of alum, known as *Roman alum*, crystallizes in opaque cubes, which retain a variable amount of aluminic sulphate, and generally have a reddish tint due to ferric oxide.

3.—A third process is resorted to in England and Germany for the purpose of turning alum schist, or *alum ore*, as it is termed, to good account. This mineral is abundant at Whitby in Yorkshire, and in the neighbourhood of Glasgow: it is a bituminous shale, found amongst the lower beds of the coal-measures, and it contains a large quantity of very finely divided iron pyrites, disseminated through its mass, which is composed chiefly of a siliceous clay. The mineral is decomposed either by exposure to the air, or, as is more usually practised, by a slow roasting of the ore, which is arranged for that purpose in alternate layers with the fuel in long heaps or ridges, which are covered more or less completely with spent ore, in order to regulate the heat and to absorb the excess of sulphuric acid. In this operation the pyrites, or ferric disulphide, is converted into ferrous sulphide, losing half its sulphur, which absorbs oxygen and is converted into sulphuric anhydride; this at the moment of its formation unites with the alumina, whilst the ferrous sulphide, gradually combining with more oxygen, is converted into ferrous sulphate, or green vitriol: $2FeS_2 + 3O_2 = 2FeS + 2SO_3$; and $FeS + 2O_2 = FeSO_4$. Great care is required to prevent the temperature from rising too high, a circumstance which would be attended with decomposition of the aluminic sulphate and loss of sulphuric acid. By the time that the roasting is complete, the mass has become greatly reduced in bulk, and is rendered porous and freely permeable to the air; in this condition the heap is allowed to lie exposed to the atmosphere, and is moistened from time to time: it is then lixiviated, the liquor is digested with metallic iron to reduce any ferric salt to

the state of ferrous sulphate, and the green ferrous sulphate is separated from the aluminic sulphate by crystallization of the liquor. The mother-liquors often yield magnesic sulphate when concentrated further.

In the Whitby alum works, in which the quantity of the aluminic sulphate much exceeds that of the ferrous sulphate in solution, the concentration is completed in leaden pans; being carried so far that the liquid, when cold, is perfectly saturated, but does not deposit any crystals. The liquid is then run off into the precipitating tank, where it is mixed with a saturated solution of potassic sulphate, or, what is better, of potassic chloride, in quantity sufficient (as found by trial on the small scale) to yield the maximum proportion of alum. The mixture is briskly agitated, and the potassic aluminic sulphate, which is sparingly soluble in cold water, is deposited in minute crystals, technically termed *alum meal* or flour. When potassic chloride is used the ferrous sulphate is decomposed, potassic sulphate is produced, and the readily soluble ferrous chloride is retained in the liquor; $2KCl + FeSO_4 = FeCl_2 + K_2SO_4$. To produce 100 parts of crystallized alum, between 18 and 19 parts of potassic sulphate are required, or about 16 parts of potassic chloride. The mother-liquor is drained off and preserved, and the crystals, which have a reddish-brown colour from adhering iron, are twice washed by subsidence with a small quantity of cold water, being well drained after each washing. The crystals are then dissolved by heat in as small a quantity of water as possible, and the solution is run off into crystallizing barrels, which in ten days or a fortnight are taken to pieces; the crystalline mass is broken into fragments, drained, and sent into the market.

In the Scotch alum works at Campsie, in the neighbourhood of Glasgow, alum meal is not formed; but the hot liquor from the evaporating pan is run into a stone cooler, in which the necessary quantity of dry potassic chloride has been placed. The liquid is thoroughly agitated and left to cool; on the sides of the vessel large crystals of alum are formed in four or five days. The mother-liquor is then drained off, and the crystals are afterwards washed and recrystallized twice.

Where ammonic sulphate can be readily and cheaply obtained, it is sometimes substituted for potassic sulphate in the manufacture of alum, as the double salt which it forms with aluminic sulphate crystallizes with almost as much facility as the potassium salt; it constitutes what is known as *ammonia alum*. Indeed, for the purposes to which alum is applied, neither the potassic

nor the ammonic sulphate is essential; the object proposed in the manufacture of alum being to obtain a salt of aluminium which, by the facility with which it crystallizes, can be freed from iron and from earthy impurities.

A number of other salts may be procured which have the same crystalline form as potassium alum, and are similar to it in constitution: for example, potassic sulphate may be replaced by sodic sulphate, when a sodium alum is formed, but the compound is much more soluble than potassium alum: in like manner the place of the aluminic sulphate may be supplied by ferric, chromic, or manganic sesquisulphate, forming a remarkable series of isomorphous compounds, some of which are enumerated in the annexed table:

Potassium alum . . .	$K_2Al_24SO_4.24OH_2$
Sodium alum	$Na_2Al_24SO_4.24OH_2$
Ammonium alum . .	$(NH_4)_2Al_24SO_4.24OH_2$
Iron alum	$K_2Fe_24SO_4.24OH_2$
Chromium alum . . .	$K_2Cr_24SO_4.24OH_2$
Manganese alum . . .	$K_2Mn_24SO_4.24OH_2$

Besides these true alums, a number of aluminic double salts may be formed with the sulphates isomorphous with that of magnesium; they crystallize in fine silky needles. A native sulphate of aluminium and manganese was stated by Kane and by Apjohn to contain 25 molecules of water. A similar salt of iron has been met with in the native state. These fibrous salts, according to How, contain only $22OH_2$, so that the formula of the manganese salt would be $MnAl_24SO_4.22OH_2$.

Ordinary alum has a sweetish, astringent taste; it is soluble in about 18 parts of cold water, and in less than its own weight of boiling water. The solution has a strongly acid reaction, and dissolves iron and zinc with evolution of hydrogen. When heated, this salt first melts in its water of crystallization, which amounts to 45·51 per cent. of its weight; as it loses water it froths up, and forms a tough, tenacious paste, which is ultimately converted into a voluminous, white, infusible, porous mass of anhydrous or *burnt alum*. If crystallized alum be submitted to a regularly increasing heat, a certain proportion of the water contained in it is readily driven off: thus by a temperature of 100° (212° F.) 10 molecules out of the 24 are expelled, and 10 more at 120° (248° F.). If the salt be now heated to 180° (356° F.) it loses 3 more OH_2, and at 200° (392° F.) it is rendered anhydrous and insoluble in water (Gerhardt). According to Naumann (*Deut. chem. Ges. Ber.*, 1875, viii. 1630) an aqueous solution of potash alum when heated at 100° (212° F.) is decomposed, and a white precipitate formed

containing a larger proportion of alumina than the normal alum. It dissolves readily in a solution of potassic hydrate, but only with difficulty in concentrated hydrochloric acid. By ignition, alum loses a great part of its acid.

Alum is largely employed in dyeing: when used in this process, sodic carbonate is gradually added to its solution as long as the precipitate is redissolved on agitation, or until two-thirds of the acid have been neutralized. The solution thus formed contains therefore a mixture of 3 salts, viz., $Al_2O_3SO_3 + K_2SO_4 + 2Na_2SO_4$. Cloths dipped into this liquid remove the redissolved alumina, and contract an intimate mechanical combination with it, by which they are enabled, as already mentioned, to retain the colours of the dye-stuffs employed. On evaporation, cubic crystals of alum are deposited from this solution, and the excess of alumina separates. A basic hydrated aluminic sulphate, $Al_2O_3.SO_3.9OH_2$, containing the same proportion of sulphuric anhydride and alumina as that formed in the mordanting liquid just described, is obtained by precipitating aluminic sesquisulphate incompletely by caustic ammonia; it is a white insoluble powder. A white earthy-looking mineral termed *aluminite*, said to have the same composition as this basic sulphate, is found near Newhaven.

Alums containing selenic acid in place of sulphuric acid have been prepared. Of these *selenic alums*, the potassic and ammonic alums crystallize easily, the sodic alum with greater difficulty (O. Petersson, *Deut. chem. Ges. Ber.*, 1873, vi. 1466).

(737) **ALUMINIC PHOSPHATES.**—Several minerals occur, into the composition of which aluminic phosphate enters. The blue *turquoise* is a hydrated native phosphate, $Al_4P_2O_{11}.5OH_2$, or $2Al_2O_3.P_2O_5.5OH_2$, coloured by copper and iron. *Gibbsite* which was formerly considered to be an aluminic hydrate was found by Hermann to consist of a hydrated phosphate of the metal, mixed with a variable proportion of hydrated alumina. Aluminic phosphate, $Al_2P_2O_6$, may be prepared artificially by mixing a solution of hydric disodic phosphate with one of alum; the precipitate must be well washed. If this precipitate be redissolved in an acid, and ammonia be added, the precipitate which falls has, according to Rammelsberg, the composition, $4Al_2O_3.3P_2O_5.18OH_2$. *Wavellite* is a mineral which crystallizes in radiating tufts of needles; according to Berzelius, it is a combination of aluminic fluoride with the last-mentioned basic aluminic phosphate, $3(4Al_2O_3.3P_2O_5.18OH_2).Al_2F_6$. The mineral *amblygonite* is a combination of fluoride and basic aluminic phosphate with trilithic phosphate. *Lazulite*, $2(3[CaMgFe]O.P_2O_5).(4Al_2O_3.3P_2O_5).6OH_2$, is a blue mineral composed of another double phosphate which contains the same aluminic phosphate, coloured by basic phosphate of iron (Rammelsberg).

Aluminic phosphate, in its hydrated form, is readily soluble in hydrochloric acid. Its solution may be precipitated by potassic hydrate, but the precipitate is redissolved by an excess of the alkali. In the operations of analysis it is often necessary to separate phosphoric acid from alumina: this is most readily effected

by Chancel's method, in which the solution in nitric or acetic acid, perfectly freed both from hydrochloric and sulphuric acid, is mixed with an acid solution of bismuthous nitrate (516). Phosphoric acid is thus precipitated as bismuthous phosphate, $Bi'''PO_4$, and the whole of the aluminium remains in solution. A more convenient process, however, is to dissolve in hydrochloric acid, and, after diluting, adding first tartaric acid and then ammonia in excess. The clear liquid should now be mixed with magnesic mixture and allowed to stand 24 hours: in order to completely free the precipitate thus obtained from alumina, it is redissolved in hydrochloric acid, and after addition of tartaric acid and ammonia again precipitated as ammonic magnesic phosphate. The alumina may then be estimated in the solutions, which retain the whole of it.

(738) **ALUMINIC SILICATES.**—The compounds of silica with aluminium are numerous and important. All the varieties of clay consist of hydrated aluminic silicate, more or less mixed with other matters derived from the rocks which, by their disintegration, have formed the clay. Clay is, in fact, the result of the combined action of air and water upon felspathic and siliceous rocks, and therefore necessarily varies considerably in composition. The fundamental constituent of the more important varieties of clay, according to the researches of Brongniart, Malaguti, Schloesing, and others, is represented by the formula $Al_2O_3.2SiO_2.2OH_2$. This appears to be the composition of the fire-clay of the Staffordshire coal-measures. The ordinary varieties of clay, however, contain fragments of undecomposed rock, a certain proportion of potassium, and variable amounts of silica in the hydrated condition, mixed with lime, magnesia, and oxides of iron; the character of the clay is materially modified according as one or other of these ingredients predominates. The intermixture of lime, magnesia, or ferric oxide with the clay, in any considerable quantity, greatly increases its fusibility, diminishes its plasticity, and causes it to be more readily attacked by acids: whilst an excess of silica renders it less fusible.

Pure clay, when moist, forms a tenacious, plastic mass, which is insoluble in water, but may readily be diffused through it in particles which are in an extreme state of subdivision; the deposit, when freed from the excess of water, resumes its plastic character. This paste, when slowly dried, and exposed to a higher temperature, shrinks very much, and splits into masses which are extremely hard, but they do not undergo fusion in the furnace. Pure hydrated aluminic silicate is very slowly acted upon by hydrochloric or by nitric acid, but it is decomposed when heated with concentrated sulphuric acid: upon this fact one of the processes for preparing alum (736) is founded. A gentle roasting of the clay, previous to the addition of the acid, frequently favours its disintegration; but ignition at a high tem-

perature renders it proof against the action of acids, except hydrofluoric. A strong solution of potassic hydrate dissolves unburnt clay very slowly; but if the hydrated alkali in excess be fused with clay, the resulting mass is easily soluble in water.

Clay emits the peculiar suffocating odour known as argillaceous when breathed upon or slightly moistened: its presence in any soil may be roughly but readily distinguished by the absorbent quality which it exhibits when applied in a dry state to the tongue or the lips; it adheres to them strongly, and absorbs the saliva from their surface. This absorbent property of clay causes it to retain ammonia in the soil to an extent which is of great importance to growing plants, and, as Way has shown, it arrests the ammoniacal portions of the manure applied to the surface, and thus not only ministers to the growth of the crop, but exerts a very important purifying influence upon water impregnated with organic and other substances, which find their way slowly through the soil. Indeed, mere agitation of such water with finely divided clay is sufficient to remove a considerable amount of the organic and saline matter previously in solution. It was found that both sulphate and chloride of ammonium were partially decomposed by the lime of the clay, the ammonia being retained, whilst a corresponding amount of calcic sulphate or chloride was formed in the solution. Clay also exerts a similar decomposing action upon potassic nitrate.

(739) **Varieties of Clay.**—The most important varieties of clay are the following:

1.—The celebrated *kaolin*, or porcelain clay of China, is a very pure white clay, furnished by the decomposition of a granitic rock, the constituents of which are quartz, felspar, and mica, the felspar having gradually disintegrated into this substance. A similar description of clay is obtained near St. Austel, in Cornwall, and at St. Yrieix, near Limoges, in France. It is in these cases chiefly produced by the disintegration of a rock known to geologists as *pegmatite*, which is, in fact, a species of granite in which mica is almost wanting, and quartz present in but small quantity. The *Cornish stone* used by the porcelain-makers is the same rock in a less advanced state of disintegration. The plasticity of kaolin is much less than that of the clay derived from the disintegration of the secondary rocks.

2.—*Pipeclay* is a white variety of clay, which is nearly free from iron. That of the Isle of Purbeck, in Dorsetshire, where it occurs nearly at the base of the clay deposits, is preferred: it is used in the manufacture of tobacco-pipes without any addition.

Pipeclay melts before the oxyhydrogen blowpipe to a transparent, nearly colourless glass.

3.—The *blue clay* of Devonshire and Dorsetshire is highly prized, as it is eminently plastic. The organic matter to which it owes its colour is destroyed when heated, and it yields a white paste when fired. It is employed as one of the materials in the manufacture of porcelain. The upper beds of this clay frequently contain a large proportion of sand mixed with the plastic material, and are well suited for making salt-glazed stoneware without further admixture.

4.—When the portion of calcic carbonate in a clay is considerable, it constitutes what is known as a *marl;* if the aluminous constituent preponderate, it forms an aluminous marl; if calcic carbonate be in excess, it is a calcareous marl. The aluminous marls are extensively used in the manufacture of the coarser and more porous kinds of pottery.

5.—*Loam* is a still more mixed substance, belonging to the more recent alluvial formations: it is the common material of which bricks are made; its red or brown colour is derived from the large proportion of ferric oxide which it contains.

6.—*Yellow ochre* and *red bole* are clays which derive their colour from ferric oxide, which is present in them in large quantity.

Halloysite is a white hydrated aluminic silicate which greatly resembles kaolin in appearance, but it is destitute of any plastic character, and is therefore unfitted for the manufacture of porcelain. *Fuller's earth* is a porous aluminic silicate which strongly absorbs oily matters; and if made into a paste with water, and applied to any spot of grease upon a board or cloth, as it dries, it removes most of the oil by capillary action. It is found abundantly near Reigate, in Surrey, as well as in other localities in England.

The following table exhibits the composition of some of the more important varieties of clay used in the arts. The first two are results obtained by Ebelmen and Salvetat; the others are from analyses executed in Richardson's laboratory, and are quoted in the second volume of the English translation of Knapp's *Technological Chemistry:*

	Washed kaolin.			Stourbridge fire-clay.	Pipe-clay.	Sandy clay.	Blue-clay.	Brick clay.
	Chinese.	St. Yrieix.	Cornish.					
Silica	50·5	48·37	46·32	64·10	53[illegible]	66·68	46·38	49·44
Alumina ...	33·7	34·95	39·74	23·15	32·08	26·08	38·04	34·26
Oxide of Iron	1·8	1·26	0·27	1·85	1·35	1·26	1·04	7·74
Lime	...	...	0·36	...	0·40	0·84	1·20	1·48
Magnesia ...	0·8	trace	0·44	0·95	trace	trace	trace	5·14
Potash and soda ...	1·9	2·40	12·67					
Water ...	11·2	12·62		10·00	12·08	5·14	13·57	1·94
	99·9	99·60	99·80	100·05	99·49	100·00	100·23	100·00

Besides these amorphous aluminic silicates, there are many which occur in a crystalline form. *Disthene,* or *cyanite,* is a blue-coloured soft mineral of this kind, $Al_2O_3.SiO_2$.

(740) **Other Aluminous Minerals.**—The *zeolites* are hydrated double silicates in which the principal bases are alumina and lime. They boil up when heated upon charcoal before the blow-pipe (hence their name, from ζέω, to boil), and are dissolved by acids, leaving the silica in a gelatinous state. In these minerals the lime is frequently replaced more or less completely by ferrous oxide, by magnesia, or by the alkalies. They are often very beautifully crystallized. *Analcime,* $Na_2O.Al_2O_3.4SiO_2.2OH_2$, is one of these minerals; it crystallizes in cubes. *Stilbite* crystallizes in radiated needles, and has the composition of hydrated labradorite, $CaO.Al_2O_3.6SiO_2.6OH_2$. *Prehnite* crystallizes in six-sided prisms; it may be represented by the formula, $2CaO.Al_2O_3.3SiO_2.OH_2$.

The varieties of *felspar,* $M'_2O.Al_2O_3.6SiO_2$, are likewise double silicates of aluminium with potassium, sodium, lithium, or calcium. Potassium-felspar, the *adularia* or *orthoclase* of mineralogists, and the *petuntze* of the Chinese potters, is sufficiently hard to scratch glass; it is used as a glaze in the manufacture of the finest kinds of porcelain. Felspar requires the most intense heat of the porcelain furnace for its fusion, when it forms a white milky glass. Sodium-felspar, from its usual white colour, has received the name of *albite.* The felspar containing lithium constitutes *petalite.* Common, or potassium-felspar, crystallizes in oblique rhombic prisms. *Labradorite* is a double aluminic silicate, analogous to felspar, but it contains calcium instead of the alkali-metals: it crystallizes in doubly oblique prisms belonging to the sixth system.

These minerals, by disintegration, yield the porcelain clay, or kaolin.

Felspar not only forms the regularly crystallized minerals just mentioned, but it occurs mingled with quartz, and other crystallized minerals: it is indeed one of the most abundant constituents of many of the older rocks. *Granite,* for example, is a rock consisting of intermixed crystals of quartz, felspar, and mica. When it contains hornblende instead of mica, the term *syenite* is given to it. *Gneiss* contains the same components as granite, but it has a more stratified appearance, as the mica occurs more in layers. *Porphyry* consists chiefly of compact felspar, with crystals of felspar disseminated through it; it is often red or green, and takes a fine polish. *Basalt* is a dark-coloured

volcanic rock, consisting of compact felspar-containing crystals of augite. When the place of the felspathic constituent is supplied by labradorite (or calcium felspar), the basalt is called *dolerite*. *Trap*, or *green-stone*, is a very tough, compact, igneous rock, of a dark-greenish or brownish-black colour; it is composed of an intimate mixture of felspar and hornblende. If it contain sodium-felspar (albite), the rock is known under the name of *diorite*. *Trachyte* is a volcanic rock also consisting chiefly of felspar, less compact than either porphyry or basalt. The porous *pumice-stone* of volcanic districts is probably altered felspar; it contains a much smaller proportion of alkali than the crystallized mineral. Melted pumice constitutes *obsidian*, or volcanic glass.

Garnet, which usually crystallizes in rhombic dodecahedra, and *idocrase*, which crystallizes in square prisms, are basic double silicates of calcium and aluminium, in which part of the lime is displaced by other protoxides, and the alumina by sesquioxide of iron, $3(CaMgFeMn)''O.(AlFe)'''_2O_3.3SiO_2$. In *pyrope*, which is a species of garnet found in Bohemia, the colouring matter is partly chromic oxide. These minerals have a hardness greater than that of quartz.

The different forms of *mica* are also double aluminic silicates, which contain in addition a small quantity of water and some alkaline fluoride. *Uniaxal* mica consists chiefly of magnesic and aluminic silicate, $4(MgKFe)O.(AlFe)_2O_3.4SiO_2$. In *biaxal* mica, $(KFe)O.3(AlFe)_2O_3.6SiO_2$, on the other hand, potassic silicate predominates. *Lepidolite* is a variety of biaxal mica in which lithic silicate takes the place of potassic silicate.

Another important aluminic magnesic silicate is *chlorite*, $4(MgFe)O.(AlFe)_2O_3.2SiO_3.3OH_2$, which occurs both massive and in crystals with a granular fracture; it is of a green colour. In the massive form of chlorite slate, it occurs as one of the widely distributed primitive rocks. There are many varieties of slate. *Roofing slate* is an argillaceous rock which splits readily into thin laminæ. *Mica slate*, as its name implies, contains particles of mica, to which it owes its glistening appearance. *Hornblende slate* contains hornblende in place of mica, and has little lustre.

(741) **Porcelain and Pottery.**—In the preparation of earthenware, the material employed is required to possess a plasticity equal to that of red-hot glass, and yet to be capable of being rendered sufficiently firm and hard by heat to resist the mechanical violence to which it is necessarily liable.

The basis of earthenware, porcelain, and china, is aluminic

silicate: it possesses the plasticity required, and when heated assumes a great degree of hardness. Pure aluminic silicate, however, contracts greatly and unequally on drying: the utensils made from it would consequently be liable to crack during their desiccation; in order, therefore, to diminish the amount of this contraction, an addition of some indifferent powder, such as ground flint, is made; whilst to compensate for the loss of tenacity thus occasioned, and which is particularly experienced in the use of the fine clays employed for porcelain, some fusible material is added, which, at the temperature required for firing, undergoes vitrification, and greatly assists in binding the mass together. According to the greater or less proportion of these fusible materials, the ware is more or less translucent, and more or less subject, like glass, to crack on the application of sudden changes of temperature.

The articles which have passed once through the kiln, and have thus acquired firmness, are rough and uneven, and the coarser kinds of ware are very porous. It is usual, after the first firing, in order to give smoothness and uniformity to the surface, as well as to render the body of the ware impermeable to moisture, to cover it with a kind of flux or glaze, which melts at a lower temperature than the material composing the ware itself; and in order to melt the glaze the articles are a second time passed through the kiln.

The materials employed in the fabrication of porcelain and earthenware are, clays of various degrees of purity and fineness, ground felspar, calcined flints or sand, burnt bones, chalk, and sodic or potassic carbonate; they do not, therefore, differ much from those which are employed in glass-making except in the great preponderance of aluminic silicate. The varieties of pottery or earthenware are numerous: the following include those which are of the most importance:

1.—*Porcelain, or China.*—This is the finest and most valuable description of ware: it is distinguished from ordinary earthenware by the composition of the paste from which it is formed. The materials are selected with great care, in order that they may give a colourless mass after firing. Porcelain consists mainly of two classes of materials, one of which, the clay, is plastic, and is infusible at the temperature employed to fire it; the other (chiefly calcic and potassic silicate) softens and becomes vitrified, forming a kind of cement which binds the clay firmly together, and thus produces a translucent mass; this when broken appears to be of a uniform texture throughout, and is impervious

to liquids. Much judgment is required in the due proportioning of the fusible and infusible materials.

The celebrated Sévres porcelain resembles the original Chinese ware, of which indeed it is an imitation. Regnault states the composition of the paste used at Sévres for ornamental purposes to be the following:—Washed kaolin, 62 parts; Bougival chalk, 4; Aumont sand, 17; quartzose felspar, 17. These ingredients are carefully levigated and then thoroughly incorporated. As, however, the composition of the kaolin varies, the proportion of the other materials must also be varied, so as to obtain a porcelain of uniform composition.

In order to give a smooth surface to the ware, a glaze similar in composition to the fusible material is used. The glaze employed at Sévres consists of a mixture of felspar and quartz. It is transparent, and rather more fusible than the body of the ware, but becomes thoroughly incorporated with it, and from its similarity in composition it expands and contracts by heat uniformly with the paste which it covers; hence it is not liable to crack and split in all directions in the manner which is so commonly observed in the glaze of the more ordinary kinds of earthenware.

The China of Berlin and Meissen is very similar in composition to that of Sévres: these constitute what is termed hard, or true porcelain.

English porcelain usually contains, in addition to the Cornish clay and felspar or flint, a large proportion of burnt bones; the glaze, which is transparent, usually contains both borax and plumbic oxide to increase its fusibility. English porcelain is softer than the Chinese, French, or German porcelain, and constitutes one variety of what the French term *porcelaine tendre*, the manufacture of which is now rarely practised in France.

2.—*Stoneware* is a species of porcelain in which the body of the ware is more or less coloured, less care being taken with regard to the purity of the material. It generally contains more oxide of iron, and consequently is somewhat more fusible than the best porcelain, and is usually salt-glazed in a manner shortly to be described. *Wedgwood-ware* is a fine description of stoneware.

3.—*Fine Earthenware.*—Articles of this description are very extensively manufactured in the Staffordshire Potteries, and constitute the ordinary table-service of this country. The Devonshire and Dorsetshire clays are those chiefly made use of; they are mixed with a large portion of ground flints, and yield an infusible paste which burns nearly white. The body of the ware is not fused in the firing, but it is rendered impervious to liquids by means of a fusible lead glaze.

4.—*Common Earthenware* is made of an inferior and more fusible description of clay: both this kind of ware and the foregoing one crack easily on the sudden application of heat.

5.—The coarsest description of clay goods are bricks, tiles, flowerpots, and similar articles.

6.—Articles which are required to stand a high temperature, such as fire-bricks for lining furnaces, muffles, pots for the fusion

of glass, crucibles for melting steel, and the Hessian crucibles so largely in demand in the laboratory, are made of a pure, infusible siliceous clay, the shrinking of which during drying is diminished by the addition either of burnt clay of the same description, or of, what amounts to the same thing, broken pots of the same material, which are reduced to a fine powder and incorporated with the paste. Good fire-ware is nearly white: if coloured, the presence of oxide of iron would be indicated, and this would render it fusible. Bauxite, a mineral containing but little silica, when mixed with a little clay and a small proportion of plumbago can be made into bricks which are exceedingly refractory, and resist the solvent action of iron slags in a remarkable degree.

The following table gives the composition of some of the most important varieties of china and pottery ware:

	Porcelain.					Wedgwood ware.	Lambeth-stone-ware.	Hessian crucible.
	Chinese.	Berlin.	English.	Sèvres.	Meissen.			
	C.Cowper.	Wilson.	Cowper.	Laurent.	Laurent.	Salvetat.	Salvetat.	Berthier.
Silica	71·04	71·34	40·60	58·0	57·7	66·49	74·00	71
Alumina	...	23·76	24·15	34·5	36·0	26·00	22·04	25
Oxide of iron ...	22·46	...	1·74	...	...	0·8	6·12	2·00	4
Lime	3·82	0·57	14·22	4·5	0·3	1·04	0·60	
Alkali	2·68	2·00	5·28	3·0	5·2	0·20	1·06	
Magnesia ...	...	0·20	0·43	...	trace	0·15	0·17	
Bone earth and oxide of iron ...	...	...	15·32					
	100·00	99·61	100·00	100·0	100·0	100·00	99·87	100·0

(742) **Manufacture of Porcelain.**—For the finer kinds of porcelain much care is taken to insure the purity and minute subdivision of the constituents, as well as their intimate admixture. The clay is first ground between horizontal stones under water; it is next levigated in water, to allow the coarser particles to subside while the lighter ones remain in suspension. The finer suspended particles are then formed into a mixture of the consistence of thin cream, a wine pint of this being made to weigh 24 or 26 ounces: in this state the cream or pulp is mixed with the ground felspar, flint, or other material. Suppose, for example, that the pulp is to be mixed with ground flints; the flints are heated to redness, suddenly quenched in cold water, and then reduced by stamping and grinding them under water to an impalpable powder; this also is suspended in water, a wine pint of the mixture being made to weigh 32 ounces. The two ingredients are easily mixed in the necessary proportions by taking a given measure of each pulp and thoroughly incorporating them. The mixture thus obtained is technically termed *slip*. The slip is well agitated and allowed to subside; the deposit is drained (carefully mixing it from time to time), and dried, until it has acquired sufficient consistence to allow of its being wrought by the potter. Much labour is afterwards bestowed in working this clay in such a manner as to render it of uniform composition throughout, and to preserve it free from air-bubbles. The mixture is found to be greatly improved in quality

by being allowed to remain for some months before it is worked up, the mass being occasionally turned over and beaten. During this process of ripening, the mass undergoes a slow change, in the course of which traces of organic matter which it contains gradually become oxidized, reducing the sulphates to sulphides, in consequence of which it evolves a slight odour of sulphuretted hydrogen, and the colour of the paste becomes somewhat darker from the formation of traces of ferrous sulphide. It is of great importance in the finer specimens of ware to avoid the presence of organic matter; a single hair might spoil a delicate work of art by the disengagement of gas, and the formation of bubbles in the interior of the mass when heated.

Less labour is expended upon the coarser kinds of pottery. After the raw clay, brought from Devonshire or Dorsetshire in blocks of about 30 pounds weight (or nearly 14 kilos.), has been dried, it is ground and mixed with a certain proportion of ground flints; it is then tempered with water into a stiff paste, and passed between rollers to complete the process of fitting it for the wheel.

The mechanical operations are of the same nature in every case: and, for fashioning the clay, the *potter's wheel* is in general use. This consists of a circular slab, which can be made to revolve in a horizontal plane, either by machinery or by a treddle, or by a winch turned by a boy or girl. A mass of clay of the size required is dashed upon the moistened slab. and is worked by the hands, the wheel revolving during the whole time, so that the operation is a compound of moulding and turning; the article is finally trimmed up with a wooden tool, and the work is detached from the wheel by passing a wire between the slab and the vessel. The moulded articles are then allowed to dry for a day or two in a room heated from 32°·2 to 37°·8 (90° to 100° F.), in order to give firmness sufficient to permit them, when necessary, to be carefully turned on a lathe. After this operation has been completed, the handles and ornaments may be attached; these are made in moulds, and adhere readily by means of slip when pressed against the moulded mass, which is still moist. The articles have at this stage received the form which they are intended to retain, and are next subjected to heat in the *biscuit* furnace. It is necessary that the temperature be raised very gradually and carefully at first, lest the aqueous vapour, being formed too suddenly, should deface the vessel or injure its texture. By this first firing the different articles acquire a greater degree of firmness, and can be handled without danger of breaking, but they are in a very porous state, technically termed *biscuit*. The ware in this stage readily absorbs any solution that may be placed upon its surface, and this is the period chosen for printing the patterns or designs which the finished goods are to exhibit. The colouring matter generally consists of some metallic oxide ground up with oil of turpentine or with boiled linseed oil. Blue is usually given by oxide of cobalt; green by chromic oxide; brown by a mixture of oxides of iron and manganese; black, by black uranium-oxide; and a pink, which is much esteemed, by a combination of stannic oxide, lime, and a minute quantity of chromic oxide. In order to apply the colouring material, it is printed from copper plates on a thin unsized paper made for the purpose; this paper, while the colour is still moist, is applied to the surface of the biscuit; the design is soon absorbed by the ware, and the paper is washed off. The ware is now subjected to another baking or firing, for the purpose of fixing the colour and burning off the oil. For decorating the finer kinds of porcelain, the metallic colour is mixed with a fusible glaze containing quartz, boracic acid, and plumbic oxide melted together. The coloured glass thus obtained is then reduced to a fine powder by levigation, and ground up with some volatile oil, in which form it is laid on in the desired pattern by means of a hair pencil. After the glazing has been completed, it is fired at a moderate heat in a muffle. In the finer kinds of decoration, the application of the colouring matter requires the

nicest management. For details upon this point (and indeed upon most others connected with the art of Pottery), the reader is referred to Brongniart's great work *Sur les Arts Ceramiques*. After the application of the colouring material, the ware still remains far too porous for use, so that it is necessary to glaze it.

The glaze for fine porcelain is prepared by levigating quartz and felspar with water, so as to form a mixture of the consistence of cream; to this a little vinegar is added, to favour the suspension of the finely divided particles. Each article is then dipped separately into the mixture. The porous mass quickly absorbs the moisture, leaving a thin uniform film of glaze upon the surface. The goods thus prepared are then enclosed in vessels made of fire-clay, termed *seggars*, and are exposed to the most intense heat attainable in the porcelain furnace.

In glazing ordinary earthenware a similar process is adopted, but the temperature of firing is below that required in the biscuit furnace. The glaze usually consists of a fusible material containing a considerable quantity of plumbic oxide: a mixture of felspar, flint, flint glass, and white lead, is in common use.

The glazing of stoneware depends upon a peculiar mode of decomposition of common salt. Sodic chloride is not decomposed, either when heated by itself, or with dry silica; but in the presence of silica and some substance capable of imparting oxygen to the sodium, and at the same time of removing the chlorine with which it is united—such, for instance, as steam or ferric oxide—the salt is susceptible of decomposition at an elevated temperature; sodic silicate and hydrochloric acid, or sodic silicate and ferric chloride, as the case may be, being formed. The various utensils, having been dipped into sand and water, are placed in the kiln, and are gradually raised to an intense heat. A certain quantity of moist salt is thrown in: the sodic chloride is quickly converted into vapour, and the salt is decomposed by the silica and ferric oxide in the clay, aided by the steam produced in the combustion of the fuel in the furnace. The ferric chloride and hydrochloric acid pass off in vapour with the excess of salt employed, whilst the sodic silicate fuses upon the ware, and renders it impervious to liquids. The reactions may be thus represented:

$$OH_2 + 2NaCl + SiO_2 = 2HCl + Na_2O.SiO_2; \text{ and}$$
$$Fe_2O_3 + 6NaCl + 3SiO_2 = Fe_2Cl_6 + 3(Na_2O.SiO_2).$$

It is worthy of remark, that although clay contracts very evenly by heat when its density is uniform throughout, yet if its density be unequal in different parts, the contraction is also unequal; hence though a vessel may issue smooth and well finished from the workman's hands, it often assumes a striated and uneven appearance during the process of firing; and if a stamp be impressed upon clay while soft, and the whole surface be shaved away until no further impression is visible, the mark of the stamp reappears after baking, in a manner more or less distinct.

(743) **ULTRAMARINE.**—Alumina enters into the formation of the pigment ultramarine, so highly prized for the purity and delicacy of its blue colour, and for its permanence when exposed to light and air, although mixed with oils, and subjected to the action of lime or of alkalies. This valuable colouring material was formerly obtained exclusively from lapis lazuli by a tedious process, which consisted in gently calcining the stone, broken into fragments of the size of hazel-nuts; the heated fragments were then quenched in vinegar, by which they were rendered

more friable, and were deprived of adhering calcic carbonate: they were next subjected to a patient levigation with a thin syrup of honey and dragon's-blood; were then made into a paste with a resinous cement; and after allowing this to remain undisturbed for some days, the ultramarine was extracted from it by suspension in hot water and subsidence.

Ultramarine is now, however, manufactured artificially upon a large scale, chiefly in Germany; and, amongst other applications, it is extensively used in paper-staining. The following process answers well upon the small scale:—100 parts of finely washed kaolin, 100 of sodic carbonate, 60 of sulphur, and 12 of charcoal, are intimately mixed, and exposed in a covered crucible to a bright red heat for three hours and a half. The residue, which should not be in a fused condition, is of a green colour: this green ultramarine is usually prepared on the large scale by igniting a mixture of kaolin, sodic sulphate, and charcoal. The product after grinding is well washed, dried, and mixed with a fifth of its weight of sulphur, and exposed in a thin layer to a gentle heat, little above that required to burn off the sulphur. When the sulphur has all been burned off, a fresh quantity of sulphur must be added, and the roasting repeated; and this roasting, with fresh additions of sulphur, must be repeated two or three times until the mass acquires a bright blue colour. Other proportions of the ingredients may be used, the temperature varying with the composition: the heat should be as high as the mass will bear, provided it is not fused. The green modification of ultramarine is also manufactured for the market. According to Philipp (*Deut. chem. Ges. Ber.*, 1876, ix. 1109), it is converted into the blue modification merely by heating it with water at 160° (320° F.), the alteration being due not to oxidation, but to the removal of a small portion of sodic sulphide. Blue ultramarines vary in tint, some being pure blue, others greenish blue, and others violet-blue, with a roseate reflex. The violet ultramarines are well adapted for use in paper-staining, as they withstand the action of the alum used in the size, which the two other tints do not.

Considerable doubt still exists as to the true nature of the colouring matter of ultramarine, which has been made the subject of study by many chemists. According to the experiments of Wilkens—who has made careful analyses of a variety of samples of the artificial product, both from his own manufactory and from other sources—ultramarine is composed of two portions, one of which is constant in composition, and which he regards as the essential colouring body; it is attacked with facility by hydrochloric acid, evolving sulphuretted hydrogen; the other portion is not soluble in the acid, and contains a variable amount of sand, clay, ferric oxide, and sulphuric acid. His analysis of the pure blue pigment corresponds nearly with the formula, $2Al_2O_3.3SiO_2.Al_2O_3.4SiO_2.Na_2S_2O_3.3Na_2S$, which would contain, in 100 parts:*

* Scheffer's analyses (*Deut. chem. Ges. Ber.*, 1873, vi. 1450), however, give very different results.

	By calculation.	By experiment.		
SiO_2	= 37·6	40·25	39·39	40·19
Al_2O_3	= 27·4	26·62	26·40	25·85
S	= 14·2	13·42	12·69	13·27
Na_2O	= 20·0	19·89	21·52	20·69

He states that the presence of iron is not essential to the production of the colour, but this is still a matter of doubt. According to Brunner, a corresponding compound, in which dipotassic sulphide is substituted for disodic sulphide, is colourless.

Ultramarine, if heated in the air, gradually assumes a dull green hue; when heated with sulphur, it is not changed; if melted with borax, sulphur and sulphurous anhydride escape, and a colourless glass remains. Sulphuric, nitric, and hydrochloric acids decompose it, and the colour is quickly destroyed. Chlorine acts still more rapidly, dissolving everything but the silica, and completely discharging the colour.

(744) **Characters of the Compounds of Aluminium.**—The ordinary salts of aluminium are colourless. They have a sweetish, strongly astringent taste, and give an acid reaction with litmus.

Before the blowpipe, the compounds of aluminium are distinguished by the formation of a pale azure blue if moistened with cobalt nitrate and gently ignited.

In solution, they give a white precipitate of hydrated alumina with *ammonic hydric sulphide,* sulphuretted hydrogen being evolved. *Ammonia* produces a bulky, semitransparent, gelatinous precipitate of hydrated alumina, which is nearly insoluble in excess of ammonia, or of its carbonate. *Potassic hydrate* dissolves it readily; and it is reprecipitated on adding solution of ammonic chloride in excess. The *carbonates of the alkali-metals* produce the same precipitate with disengagement of carbonic anhydride, but, according to Muspratt, the precipitate retains a portion of carbonic acid. *Potassic sulphate* and sulphuric acid in slight excess added to solutions of the salts of aluminium, and evaporated, furnish well-marked octahedral crystals of alum.

Estimation of Alumina.—The quantity of alumina in the course of an analysis is always estimated from the precipitate by ammonic hydrate, or carbonate or sulphhydrate; when thoroughly washed (an operation which, from its gelatinous nature, is tedious), and then ignited, it consists of the pure earth only.

(745) **Separation of Alumina from the Alkalies and Alkaline Earths.**—Supposing a magnesium salt to be present in the liquid, a solution of ammonic chloride is first added to it, unless it be powerfully acid; on the addition of caustic ammonia in slight excess, pure hydrated alumina is precipitated. Ammonic hydric sulphide is a still better precipitant, if the liquid has been previously nearly neutralized by ammonia; the precipitate is extremely voluminous, and requires careful washing. On ignition it yields pure alumina. The alkalies and alkaline earths remain in the solution which has been filtered from the alumina, and their amount may be determined by the usual methods (769 *et seq.*).

§ II. GALLIUM; Ga=69·9.

(746) **GALLIUM.**—This metal was discovered in August, 1875, by L. de Boisbaudran, in the zinc blende of Pierrefitte, in the valley of Argeles, Hautes Pyrénées, but is contained in greater abundance in that from Asturia, and still more so in the black blende of Bensberg (Rhine); it has also been found in exceedingly minute quantities in blende from other localities.

Gallium may be extracted from the finely powdered blende by dissolving it in a mixture of hydrochloric acid (5 pts.) and nitric acid (1 pt.): plates of zinc are immersed in the strongly acid liquid, which should be nearly free from nitric acid, in order to precipitate the copper, lead, cadmium, and other metals which are present. When the disengagement of hydrogen becomes very slow, the clear liquid is separated from the metallic sponge, and heated on a water-bath for a long time with a large excess of zinc, which throws down alumina, zincic oxychloride, cobalt, &c., along with the gallic oxide, as a gelatinous precipitate. This precipitate, dissolved in hydrochloric acid, is treated with zinc in precisely the same way as the original solution of blende, and the final gelatinous precipitate is again submitted to the same series of operations, when it yields the gallium in a more concentrated form. The precipitate is now dissolved in hydrochloric acid, evaporated to expel most of the excess of acid, and the dilute solution treated with sulphuretted hydrogen. The filtrate, after the addition of ammonic acetate and acetic acid, is again treated with sulphuretted hydrogen, which throws down the zinc as sulphide, and this, if in large excess, carries down with it the whole of the gallium. If the filtrate when examined spectroscopically is still found to contain gallium, more zinc salt should be added, and the precipitation by sulphuretted hydrogen continued until all the gallium is removed. The sulphides of zinc and gallium, after being carefully washed with a dilute solution of ammonic acetate saturated with sulphuretted hydrogen, are dissolved in hydrochloric acid and again precipitated by ammonic acetate and sulphuretted hydrogen so as to insure complete separation from the last traces of aluminium. The comparatively pure sulphides of gallium and zinc are finally dissolved in hydrochloric acid and separated by fractional precipitation with sodic carbonate; the gallium being thus concentrated in the first portions thrown down, together with traces of some other metals. This precipitate is then dissolved in hydrochloric acid and submitted to the same series of operations as the original solution of blende, by which all traces of foreign metals are removed, and a mixture of the pure sulphide of zinc and gallium are obtained: these are dissolved in sulphuric acid and fractionally precipitated by sodic carbonate in the cold as before. The purification is completed by one or

two treatments with excess of ammonia. In all these operations constant use is made of spectroscopic methods to ascertain when the precipitates or solutions may be rejected as being free from gallium.

When considerable quantities of material are operated on, the extraction may be much shortened by dissolving the blende, and precipitating as above described, repeating this operation. The second gallium precipitate is then dissolved in hydrochloric acid, precipitated by sulphuretted hydrogen, and after the removal of excess of SH_2 is fractionally precipitated by sodic carbonate. The first portions containing the gallium are dissolved in sulphuric acid, and the solution cautiously evaporated until it ceases to disengage white vapours of sulphuric acid. The residue dissolved in cold water is largely diluted, filtered, and boiled, when a subsalt of gallium is precipitated and should be separated from the *hot* solution by filtration. This subsalt is then dissolved in dilute sulphuric acid, the iron precipitated by potassic hydrate, and the clear solution saturated with carbonic anhydride to throw down the gallium as oxide. This is dissolved in dilute sulphuric acid, precipitated by sulphuretted hydrogen after the addition of ammonic acetate, and the clear solution boiled, when the gallium is again precipitated as a basic salt, which must be separated by filtration from the boiling solution and washed with boiling water.*

In order to obtain metallic gallium, the pure oxide or basic sulphate is dissolved in a solution of potassic hydrate and submitted to electrolysis, when it is deposited in the liquid state on the platinum plate forming the negative electrode, which should be very much smaller than the positive electrode. The gallium, after solidification, may be detached by bending the platinum plate backwards and forwards under cold water, or by removing the liquid metal by pressing the plate between the fingers under warm water. Gallium is a hard metal of a greyish-white colour which tarnishes slightly in moist air. It is not flexible or malleable, and fuses at 30°·1 (86°·2 F.), so that it melts when pressed between the fingers, forming a liquid of a silvery white colour which adheres to glass. It exhibits the phenomenon of superfusion in a remarkable degree, remaining liquid for a long time even at very low temperatures; on being touched, however, with a fragment of the solid metal, it immediately solidifies, the colour changing, and acquiring a distinctly bluish tinge as it assumes the crystalline state. The metal has been obtained crystallized in octahedra with somewhat curved faces. Its density in the solid state is 5·956 at 24°·5 (76°·1 F.), being intermediate between that of aluminium (2·6) and indium (7·4): that of the liquid at the same temperature is 6·069. Heated to redness, the metal does not sensibly volatilize, but in contact with the air becomes covered with a film of oxide. It is scarcely attacked by nitric acid in the cold, but dissolves readily when heated with hydrochloric acid, whilst a solution of potassic hydrate dissolves the metal with disengagement of hydrogen.

Salts of Gallium.—*Gallic chloride* is volatile and fuses at 70°—76° (158°—168°·8 F.). It is very soluble and deliquescent, and when free from excess of hydrochloric acid, the salt dissolves in a small amount of water, forming a clear solution, but the addition of a larger quantity of water causes an abundant white precipitate, apparently oxychloride. This dissolves slowly in cold dilute hydrochloric acid, but rapidly when heated: the neutral salt dissolves in water containing a trace of hydrochloric acid, but a precipitate is produced when it is heated. The solution in dilute hydrochloric acid, when evaporated, deposits

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* A detailed account of the methods of preparation of gallium and its properties are given in *Ann. Chim. Phys.*, 1877, [5], x. 101, and *Compt. Rend.*, 1878, lxxxvi. 475.

needles and plates which act strongly on polarized light. The corresponding *bromide* and *iodide* have been prepared: they closely resemble the chloride. Gallic sulphate is very soluble in water, but is not deliquescent. When a dilute neutral solution of this compound is boiled, nearly the whole of the gallium is deposited as a basic salt: advantage is taken of this property in the extraction of gallium from its ores. The sulphate may be obtained crystallized in nodules which are soluble in alcohol. Gallic sulphate forms an alum with ammonic sulphate, which crystallizes in octahedra, exactly resembling ordinary alum in appearance; it is soluble in cold water, and in dilute alcohol. An abundant white precipitate is formed when a solution of this alum is boiled, scarcely any of the gallium remaining in solution. This precipitate may be washed on a filter, first with boiling water, and then with cold water, without any perceptible loss of gallium; if allowed to cool in contact with the mother-liquors, however, the precipitate redissolves entirely.

From the close resemblance between aluminium alum, and that of gallium, it may be inferred that gallic oxide resembles alumina, and has the formula Ga_2O_3, whilst the chloride is $GaCl_3$ or Ga_2Cl_6.

Characters of the Salts of Gallium.—Gallium is precipitated from its solutions as oxide by the long-continued action of metallic *zinc*, especially when boiling: cadmium appears to have no action. *Ammonia* and *ammonic carbonate* give white precipitates which are somewhat soluble in excess of the precipitant. The *alkaline hydrates* also throw down gallium, but the precipitate is exceedingly soluble in excess. The *alkaline carbonates* give a white precipitate. In mixed solutions of aluminium and gallium, the former is thrown down first, whilst in mixed solutions of gallium and indium, the gallium is precipitated before the indium, so that gallium occupies a place intermediate between aluminium and indium as regards its basicity. *Sulphuretted hydrogen* produces no precipitate, even in presence of ammonic acetate and acetic acid, if the solution contains nothing but gallium, but when zinc is present the gallium is precipitated as subsulphide, along with the zincic sulphide: a similar phenomenon takes place with *ammonic sulphide*. *Baric carbonate* readily precipitates gallic oxide in the cold. *Potassic ferrocyanide* also completely precipitates gallium from strongly acid solutions.

When the induction spark, taken from the surface of a solution of a gallic salt, is examined by the spectroscope, two brilliant lines are observed in the violet, one somewhat more refrangible than K γ, the other, a broader band, is less refrangible than In β; this band (Ga α) is characteristic of gallium, and is very sensitive.

§ III. GLUCINUM: G″=9·3.

(747) **GLUCINUM**; *Density*, 2·1; *Atomic Vol. solid*, 4·43.—This metal, the *beryllium* of German writers, is extracted from the emerald, or the beryl, which consists chiefly of silicate of aluminium and glucinum, $3GO.Al_2O_3.6SiO_2$. The metal is prepared from its chloride in the same way as aluminium. *Phenakite* is a glucinic silicate, $2GO.SiO_2$.

Glucinum, according to the experiments of Debray (*Ann. Chim. Phys.*, 1855, [3], xliv. 5), is a white, malleable metal, fusible below the melting-point of silver. It does not burn in air, oxygen, or the vapour of sulphur, but it combines readily with chlorine and iodine, and also with silicon. The vapour of water is not decomposed by the metal, even when it is heated to full redness in it. Glucinum is easily dissolved by dilute hydrochloric and sulphuric acids; nitric acid, whether dilute or concentrated, acts but feebly upon it. It is, however, readily dissolved

by a solution of potassic hydrate, with evolution of hydrogen, but is not acted upon by ammonia. Glucinum forms but one oxide; there is some doubt whether this should be regarded as a protoxide, or as a sesquioxide. Berzelius adopted the latter view, but later researches favour the supposition that it is a protoxide.

(748) **GLUCINIC CHLORIDE,** $GCl_2 = 80{\cdot}3$, is prepared in the same way as aluminic chloride: it sublimes in white, silky, fusible needles, which are very deliquescent; a hydrated chloride with $4OH_2$ may be obtained in crystals. *Glucinic platinochloride,* $GPtCl_6 + 8OH_2$, forms hygroscopic eight-sided prisms of a deep yellow colour; they are soluble in alcohol, but not in ether.

(749) **GLUCINIC OXIDE,** or *Glucina* (GO = 25·3; *Density,* 2·967), is extracted from the beryl, of which it constitutes 13·6 per cent.: the mineral is reduced to a very fine powder, mixed with twice its weight of fluor-spar and gently heated with excess of sulphuric acid, by which means the silica is removed as silicic fluoride: the residue, after being heated to redness, is dissolved in dilute sulphuric acid, and ammonic sulphate is added equal to about one-fourth of the original weight of the beryl employed; most of the alumina can thus be removed by crystallization as ammonia alum, and the remainder can be got rid of by digesting the solution with metallic zinc, which precipitates it as basic aluminic sulphate. On adding sodic acetate and saturating with sulphuretted hydrogen, the zinc is precipitated as sulphide, and pure glucina can then be obtained on adding excess of ammonia to the solution (Scheffer). Freshly precipitated glucina forms with water a somewhat tenacious mass, but it does not harden like alumina when ignited. Ebelmen obtained it in crystals, by operating at a high temperature, in the same manner as upon alumina (72); it formed minute six-sided prismatic crystals of the same form as those of zincic oxide. The fixed alkalies and their carbonates dissolve glucina readily; but the dilute solution in potassic hydrate deposits glucina when boiled. Hydrate of glucina forms a bulky, white gelatinous mass, which absorbs carbonic anhydride from the air. When heated with solutions of the salts of ammonium it displaces ammonia, and is gradually dissolved. Glucinum yields several sulphates; one of these, $GSO_4.4OH_2$, crystallizes in octahedra; the other sulphates are amorphous sub-salts. It does not form an alum with potassic sulphate, but yields a double salt, in which the proportion of sulphion is divided equally between the two basyls, $K_2G_2SO_4.2OH_2$. A glucinic *aluminate* coloured with ferric oxide occurs native in the gem *chrysoberyl,* $GO.Al_2O_3$. Glucinic carbonate forms double salts with the carbonates of potassium and ammonium. A description of a large number of glucinic salts is given by Atterberg (*Deut. chem. Ges. Ber.,* 1874, vii. 472; also *Bull. Soc. Chim.,* 1874, [2], xix. 497).

(750) **Characters of the Glucinic Salts.**—The salts of glucinum have a sweet taste (the name glucinum being derived from γλυκὺς, sweet), with a slight astringency, and have an acid reaction on litmus: they are colourless, and are distinguished from those of aluminium by not yielding an alum with potassic sulphate, nor a blue colour when heated before the blowpipe with cobalt nitrate, and by giving with *ammonic carbonate* a white precipitate of glucinic carbonate easily soluble in excess of the alkaline salt. *Potassic ferrocyanide* gives no precipitate in their solutions: a white precipitate of hydrated glucina is produced by *dipotassic sulphide,* with evolution of sulphuretted hydrogen. If a hot solution of *potassic fluoride* in excess be added to a hot solution of a glucinum salt, scales of a sparingly soluble double fluoride of glucinum and potassium are formed.

Glucinum is always estimated in the form of the anhydrous earth.

§ IV. YTTRIUM, ERBIUM.

(751) **YTTRIUM**, Y = 59·7, is obtained by a method similar to that employed for aluminium and glucinum. This metal is not oxidized when heated to redness either in air or in aqueous vapour; in oxygen it burns with superb scintillations; solutions of the alkalies and the dilute acids dissolve it slowly.

Yttria, YO = 75·7, is a very rare earth, found in *gadolinite*, a mineral which occurs at Ytterby, in Sweden, and which is a silicate of yttrium, glucinum, cerium, and iron; it occurs also in *yttrotantalite* combined with tantalum, and in one or two other very rare minerals. It has usually been regarded as a protoxide, and forms a white earthy powder of density 4·842; it is insoluble in the alkaline hydrates, but the carbonates of the alkali-metals dissolve it; ammonic carbonate dissolves it still more freely.

The salts of yttrium are colourless, and they have a sweetish astringent taste; their solutions yield a white precipitate with potassic ferrocyanide, and with the soluble oxalates. The oxalate is a soft white powder, which leaves pure yttria when ignited. The most characteristic salt of yttrium is the sulphate, the crystals of which lose water at 80° (176° F.), and become milk-white, without change of form; on being put into water they do not resume their transparency.

(752) **ERBIUM**, E = 113·7.—Mosander supposed that three bases had been confounded under the name of yttria: to the more abundant of these he gave the name of yttria; the other two he distinguished as *erbia* and *terbia*. The *oxide of erbium* (EO = 129·7 ?) is feebly rose-red, and its salts have a similar colour and a sweetish astringent taste. The solutions of these salts furnish, when viewed by transmitted light, a spectrum marked by highly characteristic absorption bands.

Although Delafontaine (*Bull. Soc. Chim.*, 1866, i. 168) maintained the separate existence of erbia and terbia, the latter body would appear from the experiments of Bahr and Bunsen to be a mixture of yttria and erbia (*Ann. Chem. Pharm.*, 1866, cxxxvii. 1): this has since been entirely confirmed by the researches of Clève and Hoeglund (*Bull. Soc. Chim.*, 1873, [2], xx. 193 and 289). Erbia, according to Bahr and Bunsen, when introduced into a Bunsen burner, glows with an intense green light, which when viewed through the spectroscope furnishes a continuous spectrum crossed by brilliant streaks, so that erbia is the only solid substance known which gives a spectrum, crossed by bright lines, not due to the volatilization of the substance. The solutions of its salts give absorption spectra, in which the dark lines correspond exactly with those of the spectrum of incandescence.

Yttrium and erbium have usually been regarded as dyads, but from the close analogy of their compounds with those of

didymium and lanthanum it is not improbable that they are triads, with the atomic weights Y=92 and E=168·9. Until careful determinations of the specific heats of the metals have been made, however, the question must remain undecided.

§ V. CERIUM, LANTHANUM, AND DIDYMIUM.

(753) **Atomic Weights of Cerium, Lanthanum, and Didymium.**—These three metals have hitherto been found only in a few rare minerals, of which *cerite*, a hydrated basic ceric silicate, is the most common, and from the difficulty of obtaining them in quantity in the pure state, and the complex nature of some of their compounds, their history is at present rather obscure. These metals were long regarded as dyads with the atomic weights, Ce = 94·2, La = 93·6, and Di = 95, but Hildebrand's researches on the specific heats of these metals (*Pog. Ann.*, 1876, clviii. 71) require that they should be triads with atomic weights one and a half times those just given, in order that the atomic heats may be in accordance with Dulong and Petit's law. The numbers given by Hildebrand are Ce = 138, La = 139, and Di = 144·75. A large number of the salts of these metals have been described by Cléve (*Bull. Soc. Chim.*, 1874, [2], xxi. 196: 246).

(754) **CERIUM**, Ce = 141·3.—Metallic cerium obtained by electrolysis is malleable and can be drawn into wire. It has the colour and lustre of iron, and is susceptible of a high polish. It does not tarnish in dry air, but in moist air becomes covered with coloured films. Its melting-point is above that of antimony, but below that of silver. It burns readily, giving a brilliant light. Cerium appears to form two oxides—a cerous oxide, Ce_2O_3, and a ceric oxide, both of which yield salts with acids. The best known of these are *cerous oxalate* and the *cerous-potassic sulphate*, which latter salt is insoluble in a solution of potassic sulphate. Cerous oxalate, $Ce_23C_2O_4.9OH_2$, has been given in doses of from 0·13 to 0·26 gram, or from 2 to 4 grains, with good effect, in some cases of obstinate vomiting, and in some forms of pyrosis. Hydrated *cerous chloride*, $CeCl_3.6OH_2$, forms colourless crystals. The *ceric oxide*, CeO_2, has been obtained in colourless, transparent crystals of density 6·94; the hydrate, $2CeO_2.3OH_2$, is of a bright yellow colour. The *sulphate*, $Ce_23SO_4.8OH_2$, crystallizes in right rhomboidal prisms: it also forms hexagonal prisms of the composition $Ce_23SO_4.9OH_2$. The latter is isomorphous with *lanthanum sulphate*, $La_23SO_4.9OH_2$.

(755) **LANTHANUM**, La = 140·4, so named from λανθάνω, to lie hid, was discovered by Mosander, in 1841. Metallic lanthanum is malleable but not ductile. It resembles cerium in its general chemical characters. It appears to form only one oxide, La_2O_3, which is buff-coloured, and freely soluble in dilute nitric acid. It forms colourless, astringent salts, which give a white precipitate with the soluble oxalates.

(756) **DIDYMIUM**, Di = 142·5 (so named from δίδυμος, twin, in reference to its close association with lanthanum), is but little known in the metallic form. It readily tarnishes even in dry air, and in moist air becomes covered with a yellow film: only one definite oxide, Di_2O_3, of this metal is known, but it is probable that a higher oxide exists; this is perfectly white in the hydrated state, and is insoluble in solutions of potassic hydrate and in ammonia; it absorbs carbonic anhydride from the air. It furnishes a sparingly soluble white oxalate, and yields pale rose-coloured double sulphates with the sulphates of potassium, sodium, and ammonium. The chloride is obtained in beautiful rose-coloured crystals having the composition $DiCl_3.6OH_2$ on evaporating a solution of the oxide

in hydrochloric acid. Its solutions, when viewed through a prism by transmitted light, show a strong absorption line in the yellow, and another in the green (Part I. p. 179). A detailed description of this spectrum is given by Bunsen (*Pog. Ann.*, 1866, cxxviii. 100). Didymium salts are pink or violet-coloured, and are not precipitated at ordinary temperatures by ammonic sulphydrate.

CHAPTER XX.

GROUP IV.

MAGNESIUM—ZINC—CADMIUM.

Metal.	Symbol.	Atomic weight.	Atomic volume.	Specific heat.	Fusing point. °C.	Fusing point. °F.	Boiling point. °C.	Boiling point. °F.	Density	Electric conductivity at °C.
Magnesium ...	Mg	24	13·77	0·2499					1·743	25·47*
Zinc	Zn	65	9·10	0·0955	412	773	1040	1904	7·146	29·02
Cadmium ...	Cd	112	13·02	0·0567	228	442	860	1580	8·604	23·72

THESE metals are all volatile, and burn in the air with a powerful flame when strongly heated. They furnish but one basic oxide, and yield very soluble chlorides and sulphates; magnesic sulphide is to some extent soluble; zincic and cadmic sulphides are insoluble. These metals have a strong tendency to form basic carbonates; their corresponding salts are isomorphous.

§ I. MAGNESIUM: $Mg''=24$.

(757) **MAGNESIUM**: *Density*, 1·743.—This is usually classed with those metals the oxides of which furnish the alkaline earths, but it is much more analogous to zinc in its properties than to any other element. Magnesium is an abundant ingredient of the crust of the earth. It is found in combination in large quantities as a magnesic calcic carbonate, forming magnesian limestone, or dolomite. It is contained abundantly in sea-water as chloride, and in many springs as sulphate. It likewise enters more or less extensively into the formation of many rocks, and of a great variety of minerals.

Preparation. 1.—Bussy obtained magnesium in the metallic form by heating its anhydrous chloride with potassium in a porcelain or platinum crucible. When

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* At 17° (62°·6 F.).

cold, the contents of the vessel were digested in cold water, by which the potassic chloride and undecomposed magnesic chloride were dissolved out. The metal was left as a grey powder, which could be melted into globules.

2.—Deville and Caron (*Compt. Rend.*, 1857, xliv. 394) obtain the metal as follows:—600 grams (or 1⅓ lb.) of pure magnesic chloride are mixed with 100 grams of fused sodic chloride, and 100 of pure calcic fluoride, both in fine powder. 100 grams of sodium in small fragments are carefully mingled with the powder —the whole is thrown into a clay crucible at a full red heat, and it is then instantly covered. When the mixture has become tranquil, the cover is removed, and the fused mass is stirred with an iron rod, in order to render it homogeneous throughout, and to obtain a clean surface upon the liquid. Globules of magnesium are then distinctly visible. The crucible is allowed to cool partially, and the metallic globules are united by means of the iron rod; the melted mass is then poured upon a shovel, and the magnesium, amounting to about 45 grams (1½ ounces), is separated from the slag. The magnesium may be placed in a porcelain tray and collected into one mass by melting it in a current of hydrogen; after which it may be purified by remelting in a bath of mixed magnesic chloride, sodic chloride, and calcic fluoride. It still, however, usually retains portions of carbon, silicon, and nitrogen, from which it may be purified by careful distillation in a current of hydrogen. Wöhler has suggested the use of the double chloride of magnesium and sodium, but Sonstadt prefers to decompose magnesic potassic chloride by means of sodium; he then distils the metal in an iron crucible arranged as in the ordinary mode of distilling zinc; fig. 352. He prepares it by this method for commercial purposes on a considerable scale.

3.—Bunsen (*Ann. Chem. Pharm.*, 1852, lxxxii. 137) prepares magnesium by the electrolytic decomposition of magnesic chloride; the salt is melted in a deep covered porcelain crucible divided by a vertical diaphragm of porcelain, which extends half-way down the crucible; the electrodes are made of carbon, and are introduced through two openings in the lid, the negative electrode being notched to receive the reduced magnesium which lodges in the cavities: the crucible is brought to a red heat, and filled with the melted chloride, which is then readily decomposed by 10 cells of the zinc carbon battery (266). The principal difficulty in this operation arises from the small density of the reduced metal, which rises to the surface of the fused salt, and is liable to oxidation.

Properties.—Magnesium is a malleable, ductile metal of the colour of silver; it takes a high polish, and preserves it nearly as well as zinc at ordinary temperatures in dry air; but in a moist atmosphere it becomes slowly oxidized. Its fracture appears sometimes to be crystalline, at other times fibrous. It has about

the same degree of hardness as calc-spar. At a moderate red heat it may be melted. It may be converted into wire by heating the metal in the cylinder of a press until it softens, and then forcing it through holes in a die which forms the bottom of the press; the wire may be converted into a flattened ribbon by passing it between heated rollers. When ignited in dry air or in oxygen gas, magnesium takes fire and becomes oxidized; in the form of wire it burns easily, emitting a light of dazzling brilliancy, which has lately been employed as an artificial light for photographic purposes; the magnesia which is produced exhibits no sign of fusion. According to Bunsen and Roscoe (*Pog. Ann.*, 1859, cviii. 261), the light from a magnesium wire $0{\cdot}297^{mm.}$ in diameter gives a light equal to 74 stearin candles of 5 to the pound, the magnesium burning at the rate of 7·22 grams per hour. Hoyer states that in oxygen it gives a light equivalent to 120 candles. Deville and Caron have shown that magnesium is nearly as volatile as zinc, and that it may be distilled by heating it strongly in a current of hydrogen. A portion of the metal is carried away in suspension by the gas, and if the latter be kindled as it issues from the apparatus, it burns with a beautiful and highly luminous flame. Magnesium is but slowly acted upon by cold water, but it is rapidly dissolved if the water be slightly acidulated. It is also freely soluble in a solution of sal ammoniac. When thrown into strong hydrochloric acid it bursts into flame; yet a mixture of concentrated sulphuric and fuming nitric acid has no action on it unless it be heated. When heated in chlorine and in the vapour of bromine, of iodine, or of sulphur, it burns brilliantly. Magnesium unites directly with nitrogen, forming a transparent crystallized nitride, Mg_3N_2, which is decomposed rapidly by water into magnesia and ammonia (Deville). Geuther and Briegleb obtained a greenish yellow amorphous nitride of similar composition, by heating the metal in pure and dry nitrogen: it is immediately decomposed by water.

Magnesium reduces not only the more easily reducible metals from acidulated solutions of their salts, but also precipitates iron, zinc, nickel, and cobalt in the metallic form with evolution of hydrogen. Salts of arsenic and antimony are converted into arseniuretted and antimoniuretted hydrogen; but the salts of manganese and aluminium are not reduced by it.

(758) **MAGNESIC CHLORIDE**, or *Chloride of magnesium*, $MgCl_2=95$; *Density*, 2·177; *cryst. with* $6OH_2$, 1·562.—This salt is contained abundantly in sea-water. It may be obtained in the anhydrous condition by dissolving 1 part of magnesia in hydro-

chloric acid, and adding three parts of sal ammoniac in solution, after which the mixture is evaporated to dryness; by this means a double chloride of magnesium and ammonium is formed, $NH_4Cl.MgCl_2$, which may be evaporated without loss of acid, whilst a solution containing nothing but magnesic chloride is in great part decomposed: when the double salt is ignited in a covered crucible, the sal ammoniac is expelled, and pure magnesic chloride remains; this fuses at a red heat to a transparent liquid, and on cooling forms a silky looking mass, consisting of large flexible crystalline plates. Magnesic chloride is deliquescent, and gives out heat when dissolved in water; by evaporation at a low temperature it may be obtained in crystalline needles with $6OH_2$. It is soluble in alcohol: it forms double chlorides with the chlorides of the metals of the alkalies. If heated strongly in a current of dry ammoniacal gas, magnesic chloride is volatilized, and a white sublimate of $MgCl_2.4NH_3$ is obtained (Clark).

Dimagnesic oxydichloride; $MgO.MgCl_2$.—Attention has recently been called to this substance by M. Sorel, who finds that when mixed with water it possesses the remarkable property of 'setting,' like plaster of Paris (717), so that it can be applied to similar purposes, but furnishes a material much harder and more durable than ordinary plaster, and susceptible of a high polish. It may be mixed with 15 or 20 times its weight of other dry powders without losing its power of setting when mixed with the proper proportion of water.

(758*a*) **MAGNESIC BROMIDE**, or *Bromide of magnesium*, $MgBr_2 = 184$, occurs in sea-water, and in numerous saline springs. It is prepared in a manner similar to the chloride, which it closely resembles in properties.

(759) **MAGNESIA**, or *Magnesic oxide*; $MgO = 40$; *Density*, 3·6; *Comp. in* 100 *parts*, Mg, 60; O, 40.—The only known oxide of magnesium is a bulky, white, tasteless, infusible, and nearly insoluble powder, which when placed upon moistened turmeric-paper turns it distinctly brown. It is usually prepared by strongly igniting the artificial carbonate in a crucible, but it may also be obtained by ignition of magnesic nitrate; in this case it assumes a much denser form. Magnesia, when mixed with water, gradually combines with it, and forms a hydrate, MgH_2O_2, which absorbs carbonic anhydride slowly from the air: no sensible elevation of temperature occurs during the process of hydration. A native hydrate of similar composition occurs in crystalline scales.

(760) **MAGNESIC SULPHIDE,** or *Sulphide of magnesium,* $MgS = 56$, is but sparingly soluble in water. It may be obtained by heating magnesia in the vapour of carbonic bisulphide, or in the hydrated state as a white mucilaginous mass, by precipitating a boiling solution of magnesic sulphate with dipotassic sulphide. Magnesic sulphide is decomposed by water with formation of the hydrosulphide and hydrate: $2MgS + 2OH_2 = MgH_2S_2 + MgH_2O_2$.

(761) **MAGNESIC SULPHATE,** or *Sulphate of magnesia;* $MgSO_4.7OH_2 = 120 + 126$; *Density, anhydrous,* 2·706, *cryst.* 1·660: *Comp. in* 100 *parts, dry,* MgO, 33·33; SO_3, 66·67; *cryst.* MgO, 16·26; SO_3, 32·52; OH_2, 51·22.—This is the most important salt of magnesium. It is made in very large quantities from sea-water, either by precipitating the magnesia by means of lime, and then dissolving it in sulphuric acid; or by first crystallizing out the greater part of the common salt, after which, on evaporation, crystals of magnesic sulphate are obtained. Native magnesic carbonate is likewise sometimes acted upon with dilute sulphuric acid, and the salt crystallized by evaporation. The sulphate is also procured in considerable quantities from magnesian limestone: the rock is burned, slaked, and largely washed with water to remove part of the lime; it is then treated with sulphuric acid, and the magnesic sulphate is separated from the sparingly soluble calcic sulphate by solution and recrystallization. It is also obtained in considerable quantity from the mother-liquors of the alum works. Magnesic sulphate is a common ingredient in mineral waters. Its trivial name of *Epsom salts* is derived from the circumstance of its being abundantly contained in many springs in the neighbourhood of Epsom, from the waters of which it was at one time obtained. Magnesic sulphate is soluble in 3 times its weight of water at 15° (59° F.), and 1½ at 100° (212° F.). Its solution has a bitter, disagreeable taste. It crystallizes readily in right rhombic prisms, which are slightly efflorescent, and lose their water of crystallization when heated moderately; if the heat be intense and long continued, a part of the acid also escapes. If crystallized from a hot solution, oblique rhombic prisms with $6OH_2$ are deposited, and the ordinary crystals when heated at 52° (125°·6 F.) become opaque and lose 1 molecule, OH_2. Crystallized magnesic sulphate loses 6 of its 7 molecules of water at a temperature below 150° (302° F.), but it retains 1 molecule even at 200° (392° F.). This last molecule may be displaced by a molecule of an anhydrous salt, such as potassic sulphate, with which it forms a double salt, $MgSO_4.K_2SO_4.6OH_2$, of density 2·076, possessed of the same

crystalline form as magnesic sulphate. Ammonic sulphate forms with magnesic sulphate a similar double salt.

(762) **MAGNESIC SULPHITE,** $MgSO_3 = 104$.—This compound may be obtained in large crystals by mixing dilute solutions of magnesic sulphate and sodic sulphite. It may also be prepared by passing sulphurous anhydride to saturation into magnesia alba suspended in water, filtering, and nearly neutralizing the filtrate with magnesia. On concentration the sulphite is deposited in crystals having the formula $MgSO_3.6OH_2$.

(763) **MAGNESIC NITRATE,** or *Nitrate of magnesium* ($Mg2NO_3.6OH_2 = 148 + 108$; *Density*, 1·464), is deliquescent, and soluble in alcohol; it crystallizes with difficulty.

(764) **MAGNESIC CARBONATE,** $MgCO_3 = 84$; *Density*, 3·056.—This occurs native as a white, hard, amorphous mineral, called *magnesite*. It may be prepared artificially by precipitating a boiling solution of a magnesium salt with potassic carbonate, and dissolving the precipitate in carbonic acid water; as the gas escapes, the salt is deposited as a trihydrate, in transparent hexagonal prisms, $MgCO_3.3OH_2$: by exposure to air, the crystals effloresce and are converted into a protohydrate, $MgCO_3.OH_2$. The anhydrous carbonate may be obtained by introducing a test-tube containing a solution of magnesic sulphate into a strong glass tube containing a solution of sodic carbonate, sealing the tube, and then allowing the two solutions to mix. Crystals of magnesic carbonate are slowly deposited.

Magnesia alba, the common white magnesia of the shops, is made by precipitating a boiling solution of magnesic sulphate by a hot solution of sodic carbonate. The magnesic sulphate is allowed to remain slightly in excess, otherwise the precipitate contains a little sodic carbonate. It is deposited as a white, light, bulky powder, composed of hydrated magnesia, MgH_2O_2, combined with a quantity of hydrated carbonate, $MgCO_3.OH_2$, the amount of which may vary from 2 to 4 molecules to 1 molecule of the hydrated magnesia; it is very sparingly soluble in water. A quantity of carbonic anhydride is expelled from the mixture during the preparation of this compound.

Dolomite, $MgCa2CO_3$, when its structure is crystalline, usually consists of magnesic and calcic carbonate in the proportion of 1 molecule of each, although sometimes the proportion of calcic carbonate considerably exceeds 1 molecule. A solution of calcic sulphate decomposes magnesic carbonate at ordinary temperatures, and thus spring water originally charged with calcic sulphate may, by filtration through a bed of dolomite, become impregnated with magnesic sulphate.

A very pure magnesic carbonate is manufactured from dolomite by a process introduced by Pattinson. In this operation the mineral is finely ground and sifted, and exposed to a low red heat for 2 or 3 hours, by which the magnesic carbonate is decomposed. It is then introduced into a strong iron cylinder lined with lead, where it is mixed with water, and carbonic anhydride is forced in under a pressure of 2 or 3 atmospheres, until it ceases to be absorbed; the magnesic carbonate becomes dissolved as the so-called bicarbonate, leaving the calcic carbonate: the clear liquid, when boiled, evolves carbonic anhydride and deposits the magnesic carbonate, which is drained, and dried in a stove at a low temperature.

By mixing a solution of magnesic nitrate with an excess of a saturated solution of hydric potassic carbonate, and allowing the solution to stand for some days, a remarkable double salt is deposited in regular crystals, composed of $MgCO_3.KHCO_3.4OH_2$, but which is decomposed by redissolving it in water. The corresponding sodium salt is more stable.

A native *magnesic borate*, $3MgO.4B_2O_3$, named *boracite*, is found crystallized in cubes; it is rendered electric by heat.

(765) **MAGNESIC SILICATES.**—Silica and magnesia may be artificially combined in many proportions. A large number of minerals are formed, either wholly or partially, of magnesic silicates. *Olivine* or *chrysolite*, $2(MgFe)O.SiO_2$, is a crystallized orthosilicate, usually of a green colour, obtained from basaltic and volcanic rocks; it frequently accompanies masses of meteoric iron. *Talc* is a very soft slaty mineral, which has a formula $4MgO.5SiO_2$. *Steatite, French Chalk*, or *Soapstone* is $3MgO.4SiO_2$. *Picrosmine* is a hydrated metasilicate, $2(MgO.SiO_2).OH_2$. *Meerschaum* is another hydrated silicate, of which the formula is $2MgO.3SiO_2.4OH_2$. *Serpentine* is another hydrated magnesic silicate, $2[(MgFe)O.SiO_2].MgO.2OH_2$, in which a portion of the magnesia is often displaced by ferrous oxide. Serpentine frequently occurs in compact masses, which take a high polish, and from the beauty of its variegated colours, is often employed for ornamental purposes. It is readily attacked by acids, and occurs in sufficient abundance to be employed as a source of the salts of magnesium.

The double magnesic silicates are still more numerous. *Augite* or *pyroxene* is one of these. It is a crystalline mineral, often found in basalt and lava, and is a silicate of calcium and magnesium, portions of which metals are often displaced by iron and manganese; its formula may be written $(CaMgFeMn)O.SiO_2$. *Horn-*

blende, or *amphibole* is a silicate and aluminate of magnesium, calcium, and iron, with a variable proportion of the fluorides of calcium and potassium, $5(MgCaFeMn)O.6SiO_2.x(KCa)F_2$. It occurs sometimes in dark green or black crystals, at other times massive, disseminated through many rocks, such as syenite and porphyry, and frequently in basalt and lava. *Asbestos* and *amianthus* commonly consist of a fibrous variety of amphibole.

(766) **MAGNESIC PHOSPHATES.**—*Hydric magnesic phosphate*, $H_2Mg''_2PO_4.14OH_2$, is an efflorescent, sparingly soluble salt, which crystallizes in fine tufts of six-sided acicular prisms, when a solution of a magnesian salt is mixed with a solution of the common hydric disodic phosphate.

Ammonic magnesic phosphate, $Mg''_2(NH_4)_2PO_4.12OH_2 = 274+216$, or *triple phosphate*, as it was formerly called, is a more important compound than the foregoing one. It is formed by adding hydric disodic phosphate, mixed with ammonic chloride, to a magnesium salt; on agitation, this compound is deposited in minute crystalline grains which contain 9·796 per cent. Mg or 16·326 MgO. It furnishes a very delicate test for the presence of magnesium, as it is insoluble in water containing free ammonia, although it is taken up in appreciable quantities by pure water; and still more so by a solution of ammonic chloride. It is frequently met with as a constituent of urinary calculi, both in man and in the lower animals. On boiling a solution of magnesic sulphate with neutral ammonic phosphate, a double salt, $Mg_2(NH_4)_2PO_4.2OH_2$, is obtained in cubic crystals; it differs from the phosphate with $12OH_2$, just described, in being quite insoluble in water and in a solution of ammonic citrate. Ammonic magnesic phosphate is readily soluble in acids; ammonia precipitates it from such solutions unchanged: when ignited, it parts with its water and ammonia, and glows like alumina and zirconia as it suddenly contracts in bulk. The ignited residue contains 36·04 per cent. of MgO, and 63·96 of P_2O_5. It is frequently employed in the course of analysis for the determination of magnesium.

(767) **Characters of the Magnesium Salts.**—The salts of magnesium are colourless and have a bitter taste. Many of the magnesic minerals possess a silky lustre, and feel unctuous to the touch. Compounds of magnesium may be recognised *before the blowpipe*, by the pink tinge which they acquire when heated with cobaltous nitrate.

They give no precipitate with the *acid-carbonates of the alkali-metals* until the solution is boiled; but with *potassic* or *sodic*

carbonate they yield a white magnesic carbonate unless an ammonic salt be present, which interferes with the precipitation. *Ammonic triphosphate* gives a white crystalline granular precipitate of ammonic magnesic phosphate, which is easily soluble in acids. *Ammonic oxalate* in the presence of sal ammoniac, gives no precipitate with the magnesian salts, neither do the *soluble sulphates*. The *alkaline hydrates* throw down a white gelatinous hydrate of the earth, which is insoluble in excess of the precipitant. *Lime-water* produces a similar precipitate. *Ammonia* produces but a very incomplete precipitation of magnesia from its solutions; the gelatinous precipitate which it occasions becomes redissolved on the addition of a solution of ammonic chloride, and a double salt of magnesium and ammonium is formed.

(768) **Characters of the Metals of the First Group** (Metals of the Alkalies).—The salts of these metals when in solution are distinguished by the following characters:—1. By the absence of any precipitate on the addition of a solution of potassic or sodic carbonate: in the case of lithium, if the salt exceed two per cent. of the solution, a precipitate of lithic carbonate is liable to occur. 2. By the absence of any precipitate when sulphuretted hydrogen or ammonic hydric sulphide is added to the solution. 3. By the occurrence of a precipitate with platinic chloride in the case of ammonic or of potassic salts;* and by the formation of prismatic crystals of the platinic sodic chloride when evaporated in the presence of sodic salts.

(769) **Estimation of Potassium and Sodium.**—If the relative proportions of the potassium and sodium be not required, their combined weight is usually ascertained in the form of sulphates. They may in most cases be readily obtained in this condition by treating the solution with sulphuric acid, evaporating to dryness, and fusing the mass in a platinum crucible in which a fragment of ammonic sesquicarbonate is suspended. The excess of sulphuric acid is thus readily dissipated, and the amount of the acid combined with the potassium and sodium, is determined by precipitation with baric chloride. When ammonium salts are present with those of potassium and sodium, the amount of ammonia may be determined by distilling it off in the manner already described (683).

In order to determine the quantity of potassium and sodium in a mixture of the salts of the two metals, they should be con-

* Rubidium and cæsium would also be found in this precipitate (650, 658) if either of these metals be present.

verted into chlorides, and heated to low redness to expel moisture and all ammoniacal salts, allowed to cool, and weighed; a certain proportion of these mixed chlorides (0·7 or 0·8 gram will suffice) is then mixed with an excess of the platinic sodic chloride, evaporated to dryness over a steam bath, and the excess of the platinic sodic chloride removed by washing with alcohol of density 0·860. The crystalline residue is collected on a filter and weighed. One hundred parts contain 30·555 of potassic chloride, and correspond to 16·015 of potassium, or to 19·29 of anhydrous potash, K_2O. The quantity of sodic chloride is obtained by deducting the weight of the potassic chloride from that of the mixed chlorides employed.

(770) **The Conversion of Salts of the Alkali-metals into Chlorides**, previous to precipitation by the platinic chloride, if they are not already in that form, is rather troublesome. They may be first changed into sulphates by evaporating the solution with a slight excess of sulphuric acid, and igniting the residue; the sulphates thus obtained are to be dissolved in water and mixed with a solution of baric chloride in slight excess; the sulphuric acid is thus precipitated as baric sulphate, and the alkalies are converted into chlorides. The excess of barium must now be removed, and for this purpose a mixture of ammonia and ammonic sesquicarbonate is added to the solution after it has been filtered from the baric sulphate. The excess of barium is thus thrown down as carbonate, and the baric carbonate may then be removed by filtration. Once more the solution is to be evaporated to dryness in a platinum dish, and the residue gently ignited to expel the ammoniacal salts. The remaining mass now contains nothing but the mixed sodic and potassic chlorides.

(771) **Characters of the Metals of the Second Group** (Metals of the Alkaline Earths, including Magnesium):—1. The salts of these metals when in solution give a white precipitate on the addition of solution of sodic or potassic carbonate.—2. They yield no precipitate with ammonic hydric sulphide nor with sulphuretted hydrogen.—3. Lime-water occasions no precipitate, except in cases in which magnesium salts are present, or in which the solution contains free carbonic acid.

(772) **Separation of the Alkaline Earths from the Alkalies.**—Supposing a solution to contain salts of the alkalies and of the alkaline earths, the quantity of each base may be determined in the following manner:—An excess of a mixture of ammonia and ammonic sesquicarbonate is added to the solution, by which the

barium, strontium, calcium, and part of the magnesium are thrown down as carbonates; the liquid is filtered from the precipitate, then evaporated to dryness, and heated to expel the ammoniacal salts. The dry residue is afterwards washed with water, which dissolves out the salts of the alkali-metals: and from this liquid the proportions of potassium and sodium can be ascertained in the manner already described (769). A little magnesia is apt to accompany the salts of the alkali-metals: its presence may be detected and its quantity determined by the addition of lime-water to the solution; hydrated magnesia is precipitated, and may be collected, weighed, and added to the amount obtained from the portion which was precipitated as carbonate. The precipitation must be effected in a stoppered bottle, to exclude the carbonic anhydride of the atmosphere, which would precipitate a portion of lime with the magnesia. The excess of lime may be got rid of by the addition of oxalic acid, which occasions a precipitate of calcic oxalate that can be separated by filtration. The earthy carbonates must now be dealt with in the following manner:

(773) **Separation of Barium, Strontium, Calcium, and Magnesium.**—The alkalies having been separated in the manner just described, the carbonates of the metals which in the preceding operation were not dissolved by water are taken up with dilute nitric acid, and the liquid is largely diluted. Sulphuric acid is then added as long as it occasions a precipitate.

If the liquid originally contained no alkaline salts, it will not be necessary to convert the earths into carbonates, but the solution may be simply diluted, acidulated with nitric acid, and mixed with sulphuric acid, as before.

This precipitate may consist of baric and strontic sulphates. It must be collected, washed with boiling water and weighed, then fused with thrice its weight of sodic carbonate, by which it will be decomposed; double decomposition occurs, baric and strontic carbonates and sodic sulphate being formed. The baric and strontic carbonates, being insoluble, are separated from the soluble sodic sulphate by washing, and the carbonates of the two earths are converted into chlorides by the action of dilute hydrochloric acid. The baric and strontic chlorides are evaporated to dryness, weighed, and may then be separated with tolerable exactness by treatment with alcohol, which dissolves the strontic chloride, but leaves the barium salt unacted upon. Hydrofluosilicic acid may also be employed to separate the two earths; in the course of two or three hours the whole of the

barium is precipitated as silicofluoride, whilst the strontium remains in solution.

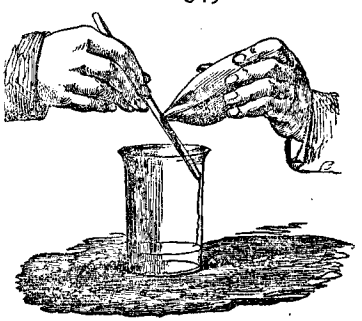
The acid liquid from which the barium and strontium have been separated is rendered slightly alkaline by ammonia, and the calcium precipitated as oxalate, by means of ammonic oxalate: this precipitate, after being well washed, is heated to dull redness, and is estimated as calcic carbonate. If the proportion of magnesium be large, a little of the calcium salt is retained in solution.

The filtrate, which may still contain magnesium, is mixed with hydric disodic phosphate, briskly stirred, and allowed to stand for twelve hours, to give time for the granular crystalline ammonic magnesic phosphate to subside: it is collected on a filter, washed with water which contains free ammonia, and estimated, after ignition, as magnesic pyrophosphate.

It will generally be found more convenient in separating the metals of the alkaline earths from those of the alkalies, in the first place to precipitate the barium and strontium by sulphuric acid from the dilute acidulated solution; then to neutralize by ammonia, and separate the calcium by the addition of ammonic oxalate; to evaporate the solution containing the salts of magnesium and of the metals of the alkalies to dryness, heating, to expel salts of ammonium; then to redissolve the residue in water, and separate the whole of the magnesia at once by the addition of lime-water in a stoppered bottle, in the manner already described.

(774) **Collection of Precipitates.**—Certain precautions in manipulation are required in transferring a solution to a filter, in order to avoid loss. In pouring a liquid from one vessel to another, a glass rod should be moistened with distilled water and brought against the edge of the vessel from which the liquid is to be poured, as shown in fig. 349. By this means, when the pouring is ended, if the rod be still kept in contact with the edge, the last drop is prevented from running down the outside of the jar or basin: the rod may then be placed in the vessel until a similar operation is again required. After the whole of the liquid has been poured off, the portion which adheres to the rod and to the sides of the vessel is washed down by a jet of water from the washing bottle, fig. 350, and the washings are added to the rest of the decanted liquid.

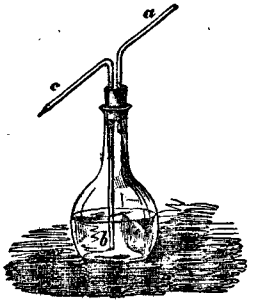
FIG. 349.



(775) **Washing of Precipitates.**—In washing precipitates, the use of a wash-bottle, that is, a flask provided with two tubes passing through the cork, as represented in fig. 350, facilitates the

operation. The tube, *a*, passes just through the cork; the longer tube, *b*, reaches almost to the bottom of the flask, terminating at *c* in a fine orifice; on forcing air from the mouth through the tube *a*, the water is expelled at *c*, and may be directed upon the filter.

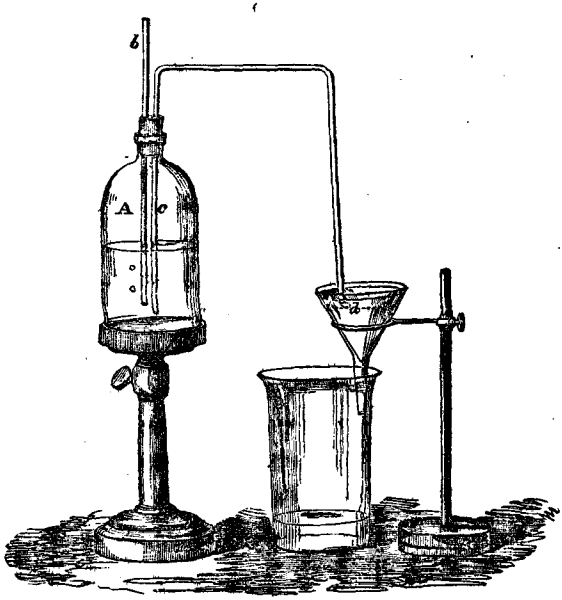
FIG. 350.



It is necessary that the filter should not project beyond the edge of the funnel, and that before any of the liquid is poured into it, the paper, after it has been placed in the funnel, should be moistened with distilled water. In washing a precipitate, the stream of water should be directed upon the upper edges of the filter, so as to wash down the saline particles, which, by evaporation of the liquid, have a tendency to accumulate there as the solution rises under the influence of capillary action.

In cases where gelatinous precipitates, like hydrated oxide of iron or alumina, are to be washed continuously for a long period, a simple piece of apparatus suggested by Gay-Lussac will be found very useful; it is merely a bottle of distilled water, A, fig. 351, which, by means of a siphon, supplies the water at a regulated level in the funnel, *d*; *b* represents a tube open at both ends, which reaches nearly to the bottom of the bottle, A; *c* is a siphon with limbs of equal length, which passes a little deeper into the bottle than *b*; the limb which dips into the funnel has its lower extremity a little recurved, to direct the pure water upwards, and the siphon can be filled by blowing gently into the bottle through the tube *b*. The funnel, *d*, is placed so that the upper edge of the filter shall be a little above the level of the lower end of *b*. Under these circumstances the filter can never overflow. As soon as the surface of the liquid in the funnel falls just below the level of the lower extremity of *b*, the siphon carries over a small quantity of water, and bubbles of air rise in the bottle, A, to supply its place. This process goes on continuously as the water flows from the filter, until A is empty.

FIG. 351.



In order to ascertain whether a precipitate has been sufficiently washed, a drop of the liquid which passes through is evaporated on a slip of glass: it ought to leave no appreciable stain or residue.

In igniting a precipitate, the paper should first be dried thoroughly; after which the portion that can be readily detached from the paper should be allowed to fall into the platinum or porcelain capsule in which it is intended to perform the ignition. The capsule is to be placed upon a smooth sheet of paper, and the filter being held at one corner with a pair of forceps, or suspended in a coil of platinum wire, is burned in such a way that the ashes shall fall into the platinum capsule: any particles of ash which may fall upon the paper are carefully transferred to the capsule.

It must not be forgotten that filtering-paper itself leaves traces of ash when burnt; but the amount of this in good specimens should not exceed about 3 grains in 1000. Before using any paper for the purposes of analysis, the quantity of ash (usually consisting of silica, lime, and traces of ferric oxide) which a given weight of it affords when burnt must be ascertained. In each analytical experiment the weight of the filter employed being approximatively known, it is easy to estimate the amount of ash which it would yield (at most but a few hundredths of a grain) and to deduct this from the gross weight of the precipitate.*

§ II. ZINC: Zn″=65·0.

(776) **ZINC**; *Density*, 6·8 to 7·2; *Fusing-pt.* 412° (773°·6 F.); *Boiling-pt.* 1040° (1904° F.) [891° (1636° F.) *Becquerel*]; *Atomic and Mol. Vol. of Vapour*, [ ]; *Rel. wt.* 65.—Zinc, or *spelter*, as it is often called in commerce, has been known in the metallic form since the time of Paracelsus. Its ores occur in considerable abundance, although it is never met with in the native state. Much of the zinc of commerce is supplied from Silesia, where the ore wrought is *calamine;* the common or rhomboidal calamine (zincic carbonate) is the most important variety, although the prismatic or electric calamine, a hydrated basic zincic silicate, is often found in the Carinthian ores: it is much more difficult of reduction. Zincic carbonate is also extensively worked in Belgium, where it is found mixed with clay. In the Mendip Hills, in Somersetshire, the zincic carbonate is associated with magnesian limestone. *Blende*, or zincic sulphide, is worked in England to some extent; it usually accompanies plumbic sulphide (or galena) in the mountain limestone. In New Jersey, *red oxide of zinc* has been found in large quantities, both massive and crystallized; the colour is due to admixture with oxides of manganese and iron. It forms a valuable ore, and is easily reduced. In the year 1860, 4357 tons of zinc were extracted from English mines.

(777) **Extraction of Zinc from its Ores—English Method.**—In the extraction of zinc, whether from blende or from calamine,

* In delicate inquiries it is desirable first to treat the filter with dilute nitric acid (1 of acid to 30 of water), by which nearly everything, except the silica, is removed, finally washing well with distilled water.

the ore is crushed between rollers, and undergoes a process of roasting; in the case of blende a preliminary mechanical treatment is required in order to separate the galena as completely as possible, as the presence of lead would occasion rapid destruction of the crucibles during the subsequent reduction of the metal. The roasting of blende is tedious, and requires to be carefully performed; the sulphur burns away as sulphurous anhydride, and the zinc becomes oxidized: $2ZnS + 3O_2$ yield $2ZnO + 2SO_2$. Calamine also yields zincic oxide when roasted, whilst carbonic anhydride and water are expelled. The roasted ore from either source is mixed with half its weight of powdered coke or anthracite, and introduced into crucibles of peculiar construction.

The method of reduction practised in England offers one of the few instances in which distillation *per descensum* is still practised:—a circular furnace, somewhat similar to that used in making glass, is employed: in this furnace six large

FIG. 352.

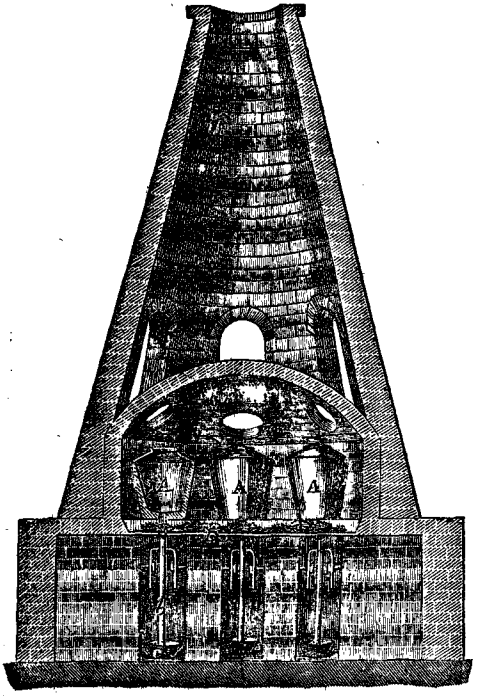
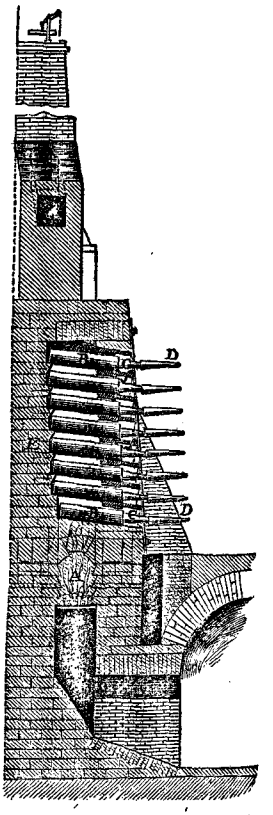


FIG. 353.



clay crucibles (three of which are represented in the section at A, A, A, fig. 352), each 1·22 metres or 4 feet high and 0·76 metre or 2½ feet in diameter, are-

arranged, three on each side of the firebars; one of these crucibles is shown in section in the figure. In the bottom of each crucible is an opening, and to this is attached a short iron pipe, which passes out through the bottom of the furnace; to this iron tube a second wider tube, *b*, about 2·44 metres or eight feet long, is fastened in such a manner as to be readily removable; beneath the open end of this tube a sheet-iron vessel, *c*, is placed to receive the zinc. The bottom of the crucible is then loosely plugged with large pieces of coke, and a charge containing from 200 to 250 kilos. (from 4 to 5 cwt.) of the mixture of calcined ore and coke is introduced into each pot, and the cover is carefully luted on. Carbonic oxide is first evolved abundantly, and burns with a blue flame at the mouth of the short iron tube; in a few hours the colour of the flame changes to brown, when the cadmium, which is more volatile than zinc, comes over, and may be condensed. When the colour of the flame changes to bluish-white, the zinc is distilling nearly pure. The flame is then extinguished by attaching the longer tube, and the metal becomes condensed partly in powder, partly in stalactitic masses, and falls down into the iron vessels, *c*, *c*, placed for its reception. The zinc, being volatile at very high temperatures, boils and distils as the operation proceeds. In order to prevent the pipe, *b*, from becoming choked, it is occasionally removed, and the zinc detached from it. The crude metal is mingled with a good deal of oxide: it is therefore re-melted, skimmed, and cast into ingots; or (if intended for rolling) into sheets, and then laminated at a temperature of about 120° (248° F.). Calamine, which contains 52 per cent. of metal, does not yield on an average above 30; the greater part of the zincic silicate, which calamine almost always contains, escaping decomposition.

(778) **Silesian Method of Extraction.**—In Silesia the distillation is effected in muffle-shaped earthen retorts, which are ranged in two rows on the same plane in a long furnace, back to back; the outer end of each retort is provided with two apertures; the lower one is employed for introducing the charge, and is afterwards carefully luted up, whilst the upper one is for receiving a bent earthen pipe which carries off the metal as it distils.

(779) **Belgian Method of Extraction.**—In Belgium the distillation is managed quite differently. The ores treated in that country are of two kinds, both occurring in a matrix of clay above a bed of dolomite: one is a red variety, containing about 33 per cent. of zinc, with a good deal of oxide of iron, but admitting of reduction at a moderate temperature; the other is a white ore, also a calamine, which contains about 46 per cent. of zinc, and requires a much higher temperature for its reduction. These two species of ore are kept distinct from each other during the process of smelting. The calamine, having been washed to remove the clay, is roasted, during which operation it loses about 25 per cent. of water and carbonic anhydride. After this it is reduced to a fine powder, and thoroughly mixed with half its weight of coal dust: this mixture is then introduced into clay retorts about three feet eight inches (1·1 metre) long and six inches or 15 centimetres in diameter; each retort is charged with about 40 lb. or 18 kilos. of the mixture of coal and roasted ore. Forty-two of these retorts are arranged in an arched furnace, in rows of six, placed one above the other. The backs of the retorts rest on notches in the wall, E, fig. 353, and are supported on a slightly higher level than the open extremities, which rest in front upon iron plates, *f*, *f*. To each retort an open, somewhat conical, cast-iron pipe, *c*, is luted; this serves as a receiver for the distilled metal, and upon each of these receivers is fitted a second receiver of sheet-iron, D, with an opening at the extremity for the escape of gas. The fire by which the retorts are heated is shown at A. In such a furnace two charges may be worked off in twenty-four hours. During the operation the small adapters, D, D, are withdrawn once in

two hours, and the liquid zinc which has condensed in the receivers is raked out into a large ladle and cast into ingots. When the distillation is complete, the residue in the retorts still retains nearly 25 per cent. of zinc, which is chiefly in the form of silicate; this portion is entirely wasted (Piot and Murailhe, *Ann. des Mines*, [4], v. 165).

The retorts in the upper part of such a furnace necessarily receive less heat than those in the lower part, and hence this process is particularly well adapted to the Belgian ores, because the poorer ones, which require less heat, can be reduced in the upper range of retorts.

(780) **Preparation of Pure Zinc.**—Commercial zinc contains a small amount of lead and of iron; minute quantities of tin and cadmium are also often present, besides occasionally traces of arsenicum, of copper and of indium. Carbon is also mentioned among its impurities, but Eliot and Storer, in their elaborate examination of the ordinary impurities of this metal, did not find it in any of the 13 specimens which they examined, although traces of sulphur were always present. The best method of obtaining the metal in a state of purity consists in passing sulphuretted hydrogen through a strong and somewhat acid solution of zincic sulphate, filtering from any precipitate which may be formed; and after boiling the solution, in order to expel the sulphuretted hydrogen, precipitating the zinc in the form of carbonate by the addition of sodic carbonate. The carbonate after being washed and redissolved in pure sulphuric acid is submitted to electrolytic decomposition, or else the dried carbonate may be converted into zincic oxide by ignition, and then distilled in a porcelain retort with charcoal prepared from loaf sugar. If an ammoniacal solution of zincic sulphate is electrolyzed, the positive electrode being a zinc plate and the negative a copper wire, pure zinc is deposited on the latter in the crystalline state.

(781) **Properties of Zinc.**—Zinc is a hard, bluish-white metal, which, when a mass of it is broken across, exhibits a beautiful crystalline fracture. It is rather brittle at ordinary temperatures, but between 100° and 150° (212° and 302° F.), it is possessed of considerable ductility and malleability, and may then be laminated and wrought with ease: at 210° (410° F.) it again becomes so brittle that it may be pulverized in a mortar. It fuses at about 412° (773°·6 F.), and volatilizes at a bright red heat: its boiling-point is estimated by Deville at 1040° (1904° F.), and by Becquerel at 891° (1636° F.): if its vapour be exposed to the air, it burns with great splendour and is converted into zincic oxide, which is deposited in copious white flocks. Zinc soon tarnishes when exposed to a moist atmosphere, and becomes covered with a thin, closely-adhering film of oxide, by which the

metal beneath is protected from further change. This property renders zinc valuable for a variety of economical and domestic purposes. If moistened with water it combines readily at ordinary temperatures with chlorine, bromine, and iodine; it is also easily attacked by all the mineral acids, and is employed for preparing hydrogen by acting on it with dilute sulphuric acid. A strong solution of potassic hydrate likewise attacks zinc if boiled with it; hydrogen being liberated, whilst zincic oxide is formed and dissolved by the alkaline solution; $Zn + 2KHO$ becoming $H_2 + K_2O.ZnO$. Zinc precipitates from their solutions most of the basylous metals less oxidizable than itself. With a solution of cupric sulphate it not only throws down the copper, but also decomposes the water, hydrogen being evolved in considerable quantity, especially if the solution be warm.

(782) **Uses of Zinc.**—The uses of zinc are daily extending. From its durability, cheapness, and lightness, it is frequently employed as a substitute for lead in roofing. It is employed as the oxidizable metal in the construction of the voltaic battery. Sheet iron coated with zinc, or *galvanized* iron as it is usually called, is also used for roofing: the iron gives strength, whilst the zinc protects it from oxidation, and it is not combustible like zinc alone. Galvanized iron is prepared by cleaning sheet iron thoroughly as in making tin-plate (924), and plunging the metal into a bath of molten zinc, covered with sal ammoniac; the surface of the zinc is by this means kept free from oxide, which is dissolved by the sal ammoniac, and the two metals unite readily. A tougher and superior article is obtained by first coating the iron plate with a very thin film of tin by a voltaic action, and then immersing the metal in the melted zinc.

Zinc has a considerable power of dissolving iron, in consequence of which it corrodes the iron pots in which it is melted: an alloy of zinc with a small proportion of iron is formed, which is less fusible than zinc, and crystallizes in large plates on cooling.

(783) **Alloys of Zinc.**—Zinc forms several valuable alloys. Of these, brass is the most important: it consists of about 2 parts of copper to 1 of zinc. German silver is brass containing a portion of nickel, to which its white colour is due. Of late years zinc in powder has been employed as the basis of a pigment well adapted to resist the action of the weather. Zincic oxide has likewise been substituted for red lead with advantage in the preparation of glass for optical purposes (637). Zinc precipitates many metals from their solutions as copper, lead, mercury, and silver; cobalt and

nickel are also completely precipitated provided the solution be ammoniacal. Iron also is thrown down to a great extent from solutions containing ammoniacal salts.

(784) **ZINCIC CHLORIDE**, or *Chloride of zinc*; $ZnCl_2$= 136; *Density*, 2·753.—This salt may be prepared by heating the metal in chlorine gas, but it is generally obtained by dissolving the metal in hydrochloric acid; the acid is decomposed, its chlorine unites with the zinc, forming zincic chloride, which is retained in solution, whilst the hydrogen escapes in the gaseous form. When this solution is heated, it loses water until the temperature rises to 250° (482° F.); it then becomes anhydrous, but remains fluid and may be heated to above 371°·2 (700° F.) without emitting an inconvenient amount of fumes; hence it is sometimes employed as a hot bath for maintaining objects at a high but measurable and regulated temperature. At a red heat it distils. Pure zincic chloride is a white, very deliquescent substance, which is fusible; it is powerfully corrosive when applied to the skin. Under the name of *Burnett's Disinfecting Fluid*, its solution has been largely used as an antiseptic, and as a preservative of wood and vegetable fibre against decay. Zincic chloride is soluble in alcohol.

Zincic chloride absorbs ammoniacal gas freely. It also unites with zincic oxide in several proportions, and forms a number of oxychlorides. Zincic chloride forms double salts with the chlorides of the alkali-metals; a concentrated solution of the zincic ammonic chloride, $2NH_4Cl.ZnCl_2$, being used for the purpose of removing the film of oxide from the surface of metals, such as zinc, iron, or copper, which are to be united by the operation of soldering. The cells of Leclanché's battery after having been in use some time deposit prismatic crystals which, according to Priwoznik, have the composition $ZnCl_2(NH_3)_2$. Zincic chloride forms crystalline double chlorides with magnesic and baric chlorides.

(785) **ZINCIC OXIDE**, or *Oxide of zinc*; ZnO=81; *Density*, 5·612; *Comp. in 100 parts*, Zn, 80·24; O, 19·76.—It is possible that the film which is formed upon the surface of metallic zinc by exposure to the air is a suboxide, but only one well ascertained oxide of the metal is known, and this is regarded as a protoxide; this oxide is occasionally deposited in furnace flues in yellowish six-sided prisms, but it is generally obtained in the form of a white flocculent powder. If zinc be thrown in small quantities at a time into a capacious clay crucible previously heated to whiteness, it burns with a brilliant flame and deposits large white

flakes of the oxide; but when thus prepared, it is mechanically mixed with particles of the metal, from which it may be separated by levigation with water; the heavier metallic portions subside quickly and leave the oxide in suspension. The process of manufacturing this oxide when it is required as a pigment, known as *zinc white*, consists in distilling zinc from clay retorts into chambers through which a current of air is maintained. The volatilized metal burns at the high temperature to which it is exposed under these circumstances, and the oxide is deposited in a series of condensing chambers. It has been attempted to introduce this white pigment as a substitute for white lead, but although the colour is permanent, and of a pure white, it does not cover so well, neither does it combine chemically with the oil necessary as a vehicle for distributing the colour, and hence it soon peels off, and allows moisture to penetrate. An impure oxide, sold under the name of *tutty*, is obtained from the flues of furnaces in which brass is melted.

Zincic oxide becomes pale yellow when heated, but recovers its whiteness as the temperature falls. It is readily soluble in acids. The hydrated oxide, ZnH_2O_2, is precipitated from the solutions of the salts of zinc by the addition of potassic or sodic hydrate, as well as by ammonia; it is redissolved by an excess of the alkaline liquid.

(786) **ZINCIC SULPHIDE**, *Sulphide of zinc*, or *Blende*; ZnS=97; *Density*, 4·1; *Comp. in* 100 *parts*, Zn, 67·01; S, 32·99.—This compound is one of the most abundant minerals of zinc. When pure it is of a pale-brown colour, but generally it is nearly black from admixture with sulphide of iron. It sometimes occurs massive, but is usually crystallized in rhombic dodecahedra, although it occurs in other forms of the regular system. Metallic zinc does not unite readily with sulphur, but if mixed with cinnabar (mercuric sulphide) and rapidly heated, the mercury is volatilized, and zincic sulphide is formed with almost explosive violence. Zincic sulphide does not fuse when heated: when roasted in the air it absorbs oxygen, and at a low temperature a large portion of it is converted into zincic sulphate; at a higher temperature sulphurous anhydride is formed, and zincic oxide is left. The sulphide is only slightly attacked by sulphuric and hydrochloric acids, but nitric acid and aqua regia dissolve it readily. When the salts of zinc are mixed with hydric ammonic sulphide, a white, gelatinous, hydrated zincic sulphide is precipitated, which absorbs oxygen quickly from the air, and is readily dissolved by acids.

(787) **ZINCIC SULPHATE**, or *Sulphate of zinc*; $ZnSO_4.7OH_2$ $=161+126$; *Density, anhydrous,* 3·681; *cryst.* 1·931.—This salt is obtained in large quantities as a residue in the ordinary process of preparing hydrogen by the action of dilute sulphuric acid upon the metal. It may also be prepared by roasting zincic sulphide at a low temperature, lixiviating the mass and crystallizing. It forms colourless four-sided prisms, which are efflorescent in dry air, and constitute the *white vitriol* of commerce. It is soluble in $2\frac{1}{2}$ parts of water at 15° (59° F.), and melts in its water of crystallization when heated; it may be obtained crystallized with 1, 2, 5, and 6 molecules of water, by varying the temperature at which the crystals are allowed to be formed. Zincic sulphate is employed medicinally in small doses, and is also prepared largely for the calico printer. It forms double sulphates with potassium and ammonium, which crystallize with $6OH_2$. Several basic zincic sulphates have also been obtained.

(788) **ZINCIC CARBONATE**, or *Carbonate of zinc*; $ZnCO_3$ $=125$; *Density,* 4·4; *Comp. in* 100 *parts,* ZnO, 64·8; CO_2, 35·2; or Zn, 52; CO_3, 48.—This is found native, both massive and crystallized, in forms derived from the rhombohedron. It is usually of a greyish or yellowish colour, forming one variety of *calamine,* which is so named from its property of adhering, after fusion, in the form of reeds, to the base of the furnace. It readily loses carbonic anhydride when ignited. No neutral zincic carbonate can be obtained from the salts of the metal by double decomposition. When a hot solution of a zincic salt is precipitated by a boiling solution of an alkaline carbonate, a hydrated oxycarbonate is formed, consisting of $8ZnO.3CO_2.6OH_2$ (Schindler). Several other basic zincic carbonates can be obtained.

The other variety of calamine becomes electric by heat; it is a hydrated orthosilicate, $2ZnO.SiO_2.OH_2$.

(789) **Characters of the Salts of Zinc.**—The zinc salts are colourless; their solutions have an astringent, metallic taste, and act rapidly and powerfully as emetics.

Solutions of zinc acidulated with a mineral acid, are not precipitated by sulphuretted hydrogen, but zincic acetate even if the solution be strongly acid with acetic acid yields a white precipitate consisting of the hydrated sulphide; they yield a white hydrated sulphide of zinc with *hydric ammonic sulphide,* a white hydrated oxide with *potassic* or *sodic hydrate,* or *ammonia,* soluble in excess of the alkali; a white basic zincic carbonate with the *carbonates of*

the alkali-metals soluble in excess of a solution of ammonic carbonate, but not in that of potassic or sodic carbonate; they also yield a white precipitate with *potassic ferrocyanide.*

Heated on charcoal in the reducing flame of *the blowpipe,* the metal is reduced and volatilized, burning into white fumes of zincic oxide. If moistened with a solution of cobaltous nitrate, and heated on charcoal in the oxidizing flame, the compounds of zinc leave an infusible green residue.

(790) **Estimation of Zinc.**—Zinc is best precipitated for analysis by potassic carbonate, the whole solution being evaporated down to dryness: the residue, which contains the zincic carbonate, is washed with boiling water, dried, converted into zincic oxide by ignition, and weighed. The oxide contains, in 100 parts, 80·24 of zinc. If ammoniacal salts be present, a sufficient excess of the potassic carbonate should be used to completely decompose the ammoniacal salts, the ammonia being thus entirely expelled as carbonate during the process of evaporation. The foregoing process is not applicable to the separation of zinc from any but the alkali-metals.

(791) **Separation of Zinc from the Alkalies and Alkaline Earths.**—This may be effected by the addition of hydric ammonic sulphide to the solution after it has been neutralized by ammonia; the zinc is thus precipitated as hydrated sulphide: it must be washed with a solution of sulphuretted hydrogen to prevent its oxidation, then redissolved in hydrochloric acid, and evaporated to dryness with excess of potassic carbonate: the soluble salts must be washed away from the zincic carbonate, which is then converted into oxide by ignition, and weighed.

The separation of zinc from aluminium and glucinum may be effected by dissolving all the bases by an excess of potassic hydrate, and adding hydric ammonic sulphide to precipitate the zincic sulphide; this may be collected and its amount determined in the manner just described.

§ III. CADMIUM: Cd″=112.

(792) **CADMIUM**; *Density,* 8·6 to 8·69; *Fusing-pt.* 227°·8 (442° F.); *Boiling-pt.* 860° (1580° F.) [720° (1328° F.) *Becquerel*]; *Theoretic Density of Vapour,* 3·869; *Observed,* 3·94; *Atomic and Mol. Vol. of Vapour,* [ ]; * *Rel. wt.* 56.—Cadmium

* One atom of cadmium (like zinc and the other metallic dyads yields) 2 volumes of vapour instead of 1 volume.

was discovered by Stromeyer, in 1818. It is occasionally found as cadmic sulphide, accompanying the ores of zinc, and is obtained as an accidental product during the extraction of the latter metal. Being more volatile than zinc, the greater part of the cadmium sublimes among the first portions of the distilled metal, from which it may be extracted by dissolving them in sulphuric acid, and precipitating the cadmium as sulphide by means of sulphuretted hydrogen: the sulphide may be dissolved in strong hydrochloric acid, precipitated by ammonic sesquicarbonate, and reduced in an earthen retort by ignition with charcoal; the metal distils over at a heat below redness.

Cadmium is of a white colour, resembling tin, and when a rod of the metal is bent it emits a crackling noise; it is so soft that it will mark paper like lead; it possesses considerable malleability and ductility, but when heated to about 80° (176° F.) it becomes very brittle, and may be powdered in a mortar with facility. Cadmium fuses at 227°·8 (442° F.), and may be obtained in octahedral crystals as it cools, or better by distilling the metal in a current of hydrogen in a combustion tube. It undergoes little change when exposed to the atmosphere at the ordinary temperature, but when thrown into a red-hot crucible it takes fire, depositing brownish-yellow fumes of the oxide. It is dissolved with evolution of hydrogen, when heated with slightly diluted sulphuric or hydrochloric acid; nitric acid dissolves it still more readily. It is noteworthy, however, that cadmium, which is powerfully attacked by nitric acid of density 1·47, becomes passive when in contact with a large surface of platinum, the action being arrested.

The addition of cadmium to the more fusible metals generally yields an alloy of low fusing-point without destroying the toughness or malleability of the compound. An alloy consisting of 15 parts of bismuth, 8 of lead, 4 of tin, and 3 of cadmium, furnishes a silver-white alloy of density 9·4: it softens between 55° and 60° (131° and 140° F.), and at about 60° (140° F.) is completely liquid; it expands a little as it solidifies. This alloy is somewhat ductile, and may be filed readily without clogging the tool; it preserves its brilliancy in the air. An alloy consisting of 1 part of cadmium, 6 parts of lead, and 7 of bismuth, melts at 82° (179°·6 F.).

(793) **CADMIC CHLORIDE,** or *Chloride of cadmium,* $CdCl_2.2OH_2$, crystallizes easily.

Cadmic iodide (density 4·576) may also be obtained in crystals which have a pearly lustre. It is anhydrous, and fuses readily on the application of

heat. This salt is easily obtained by digesting metallic cadmium with iodine and water, and evaporating the solution; it is employed for iodizing collodion for photographic purposes (127 *h*).

(794) **CADMIC OXIDE,** or *Oxide of cadmium;* CdO = 128; *Density,* 6·95; *Comp. in* 100 *parts,* Cd, 87·5; O, 12·5.—This oxide is obtained as a brown, anhydrous powder, by burning the metal in the air, or by igniting cadmic nitrate: according to Sidot (*Zeits. Chem.*, 1869, v. 606), when it is heated to whiteness in a porcelain tube, through which a current of oxygen is passed, it melts, and sublimes, condensing in the cold part of the tube in reddish crystals. A white hydrated cadmic oxide, CdH_2O_2, may be obtained by decomposing a salt of the metal by a fixed alkali; ammonia in excess redissolves it, but the potassic and sodic hydrates do not; even the anhydrous oxide is soluble in ammonia. Ammonic sesquicarbonate does not dissolve cadmic oxide either in the anhydrous or the hydrated form.

(795) **CADMIC SULPHIDE,** CdS = 144, constitutes the mineral known as *greenockite,* which occurs crystallized in six-sided prisms. It may be formed artificially by passing a current of sulphuretted hydrogen through a solution of a salt of cadmium; it greatly resembles orpiment in appearance, but is distinguished from the latter by its insolubility in ammonia and in the sulphides of the alkali-metals, and by not being volatile. It forms a bright yellow pigment highly valued both for the purity and the permanence of its tint.

(796) **Characters of the Salts of Cadmium.**—The cadmic salts are colourless, and resemble those of zinc. They may be readily distinguished by the yellow precipitate of cadmic sulphide which they yield with *sulphuretted hydrogen* in acid solutions; this precipitate is insoluble both in ammonia, in the alkaline sulphides, and in potassic cyanide, but soluble in boiling dilute sulphuric acid. *Potassic and sodic hydrates* give a precipitate of white hydrated oxide, insoluble in excess of the precipitant; *ammonia,* a similar precipitate freely soluble in excess; *carbonates of potassium, sodium, and ammonium,* a white carbonate, insoluble in excess; *oxalic acid,* a white precipitate, soluble in ammonia; *potassic ferrocyanide,* a yellowish-white precipitate, soluble in hydrochloric acid.

Cadmium compounds are decomposed in the blowpipe flame, and deposit a ring of brown cadmic oxide on the cool part of the charcoal, due to the reduction and subsequent combustion of the metal.

(797) **Estimation of Cadmium.**—Cadmium is readily separated from all the foregoing metals by the action of sulphuretted hydrogen, which causes a precipitate of yellow cadmic sulphide from an acidulated solution of the salts of this metal. This precipitate is redissolved in nitric acid, decomposed by an excess of sodic carbonate, evaporated to dryness, and well washed to free it from the soluble salts; the resulting cadmic carbonate is finally heated to redness to convert it into the oxide; 100 grains of cadmic oxide contain 87·5 of the metal.

CHAPTER XXI.

GROUP V.

METALS MORE OR LESS ALLIED TO IRON.

Metals.	Symbol.	Atomic weight.	Atomic vol.	Specific heat.	Density.	Electric conductivity 0° C.
Cobalt	Co	59	6·59	0·1069	8·950	17·22
Nickel	Ni	59	7·13	0·1086	8·280	13·11
Uranium ...	U	120	6·52		18·4	
Iron	Fe	56	7·14	0·1138	7·844	16·81
Chromium ...	Cr	52·5	7·71		6·810	
Manganese ...	Mn	55	6·86	0·1217	8·013	

THIS group includes those metals which are distinctly magnetic; uranium, however, appears to be diamagnetic. They decompose water at a red heat, and are soluble with evolution of hydrogen in hydrochloric and in dilute sulphuric acid. They each form several oxides, two at least of which, except in the case of cobalt and nickel, are soluble in acids. Sulphuretted hydrogen does not precipitate the metals of this group from solutions acidulated with the mineral acids. Corresponding salts of these metals are isomorphous (see page 354).

§ I. COBALT: Co″=59.

(798) **COBALT**, *Density*, 8·95, appears to have been first recognised as a distinct metal by Brandt, in 1733. It generally occurs in combination with arsenic, as speiss-cobalt or tin-white cobalt, $CoAs_2$, but occasionally it is found as cobalt glance, which is a compound of the arsenide and the sulphide of the metal, CoSAs. Cobalt is never met with in the native state, except in small proportion as a constituent of meteoric iron. The black oxide has been found to some extent in the Western States of America, mixed with cobalt sulphide, and with variable proportions of the oxides of nickel, manganese, iron, and copper. The ores of this metal occur chiefly in the primitive rocks, and are usually very complicated; they contain nickel, iron, and often bismuth and copper, mineralized either by sulphur or by arsenic, or by both together.

(799) **Extraction of Cobalt.**—It is not easy to obtain cobalt in a state of purity. On a small scale the ore may be treated as follows:—It is first roasted at a low but gradually increased

temperature, in order to expel the greater portion of the arsenic; after which it is dissolved in aqua regia, and evaporated to dryness to drive off the excess of acid: it is then redissolved in water, and a current of sulphuretted hydrogen is passed through the solution. Bismuth, copper, and the remainder of the arsenic are thus precipitated as sulphides. The filtered liquor is boiled to expel the excess of the gas, and a slight excess of nitric acid is added to the boiling liquid, to convert the ferrous into ferric salts; when cold, it is diluted and supersaturated with ammonia which precipitates the iron as sesquioxide, carrying with it a little cobalt, but the bulk of the cobalt remains dissolved together with any nickel which the ore may have contained.

The exact separation of cobalt from nickel is tedious. Two methods have been proposed, one by Rose, the other by Liebig (828). Rose's method is the following:—The two metals are thrown down from the ammoniacal liquid as sulphides, by the addition of ammonic hydric sulphide. The sulphides are redissolved in nitric acid, the solution is then largely diluted, and acted upon by a current of chlorine; after this it is digested in a closed vessel for 12 hours with powdered baric carbonate. The chlorine converts the cobalt into sexquioxide, which is gradually precipitated by the baric carbonate, and remains mixed with the excess of carbonate. This precipitate is again dissolved in hydrochloric acid: the barium is removed by adding sodic sulphate, and the cobalt precipitated as protoxide by sodic hydrate: the precipitate after being well washed with boiling water, is reduced in a current of hydrogen, when the metal is obtained in the form of a black, highly magnetic powder. When nickel is to be separated from cobalt for purposes of analysis, T. H. Henry recommends that a solution of bromine be substituted for chlorine gas in the foregoing process. Bromine may be used instead of chlorine in many analogous cases with great convenience.

If cobaltous oxide be reduced in a crucible lined with charcoal, a carbide of cobalt is formed, which may be obtained in a well-fused button. The crucible may be lined with charcoal by dipping it into water, and filling it completely with charcoal finely powdered, and sufficiently moistened to render it coherent when firmly beaten into the crucible; a cylindrical cavity is then scooped out of the middle of the mass, and its interior is carefully smoothed with a glass rod, after which the crucible is allowed to dry slowly. Nearly pure cobalt may be obtained by heating cobaltous oxalate in a covered porcelain crucible, which is inclosed in an earthen one having the cover luted down; the

crucibles are then exposed for an hour to the most intense heat of a forge: a well-fused button of cobalt may generally be obtained in this manner, and after fusing and rolling has much the aspect of polished iron.

(800) **Properties of Cobalt.**—Metallic cobalt is nearly as infusible as iron. It is of a reddish-grey colour, hard, and strongly magnetic. Deville states that by reducing the oxalate in a crucible lined with lime, he obtained a metallic button which yielded a wire of a tenacity nearly double that of an iron wire of the same diameter. It is slowly dissolved by hydrochloric and dilute sulphuric acids with evolution of hydrogen, and it is freely attacked by nitric acid; when exposed to the atmosphere, it is gradually converted into oxide. Cobalt is not used in the metallic state in the arts. Many of the compounds of cobalt are remarkable for the beauty and brilliancy of their colour, and are used as pigments.

The alloys of cobalt are unimportant. Its compounds with arsenic are interesting, as they supply the greater part of the cobalt employed in the arts. *Tin-white cobalt*, $CoAs_2$, when pure, contains 28·23 per cent. of cobalt and 71·77 of arsenicum, but portions of the cobalt are frequently displaced by nickel and iron. The purest specimens of this mineral are obtained from Tunaberg, and the ore from this locality is the best material to employ in preparing the compounds of cobalt. Arsenide of cobalt melts at a moderate red heat. *Bright white cobalt*, or *cobalt glance*, CoSAs, corresponds in composition to mispickel: it crystallizes in cubes, octahedra, or dodecahedra, and contains 35·54 per cent. of cobalt, 45·18 of arsenicum, and 19·28 of sulphur. These minerals are energetically decomposed by nitric acid or by aqua regia, and are readily attacked when heated in a current of gaseous chlorine. They are also decomposed when roasted in a current of air.

(801) **COBALTOUS CHLORIDE**, or *Chloride of cobalt*, $CoCl_2 = 130$; *Density*, 2·937.—This salt is obtained as a lilac-coloured anhydrous mass, by passing chlorine over metallic cobalt; it is volatile at a high temperature. By dissolving cobaltous oxide or carbonate in hydrochloric acid, and concentrating the solution until its boiling point reaches 111° (231°·8 F.), the hydrated chloride may be obtained in ruby-red octahedral crystals with $6OH_2$, of density 1·84, which are readily soluble in water and in alcohol; at higher temperatures it yields the compounds $CoCl_2.4OH_2$ and $CoCl_2.2OH_2$, both of which are deliquescent. Its aqueous solution when concentrated, or when mixed with an

excess of strong hydrochloric acid, is of a deep blue colour, but on dilution it becomes pink. This dilute solution may be used as a sympathetic ink; characters traced with it on paper, although invisible when cold, become blue by heat, and again fade as the hygroscopic moisture of the paper is restored from the air: the colours of this ink may be varied at pleasure; the addition of a small proportion of a ferric salt renders it green; a salt of zinc produces a red, and one of copper a yellow tint. Other hydrates are known containing $2OH_2$ and $4OH_2$ respectively. Anhydrous cobaltous chloride absorbs 4 molecules of ammonia, and if its solution be mixed with an excess of ammonia it deposits crystals, consisting of $CoCl_2.6NH_3.OH_2$.

(802) **COBALTOUS BROMIDE**; $CoBr_2 = 219$.—Bromine and water dissolve cobalt, and the solution evaporated over sulphuric acid deposits purple-red prismatic crystals of the *hexhydrate* $CoBr_2.6OH_2$; at 100° (212° F.) it loses water and leaves a dihydrate, $CoBr_2.2OH_2$, as a mass of purplish-blue crystals; at 130° (266° F.) it becomes anhydrous and of a bright green colour. All these compounds are deliquescent (Hartley, *Jour. Chem. Soc.*, 1874, xxvii. 301).

(803) **COBALTOUS IODIDE**; $CoI_2 = 313$.—This is prepared in the same manner as the bromide. The *hexhydrate*, $CoI_2.6OH_2$, forms large deliquescent hexagonal prisms of the colour of dark smoky quartz; the *dihydrate*, $CoI_2.2OH_2$, is a mass of green deliquescent crystals. The anhydrous iodide obtained by heating the hydrates at 130° (266° F.) is a black mass with a lustre resembling that of graphite (Hartley, *loc. cit.*).

(804) **OXIDES OF COBALT.**—There are two well-marked oxides of cobalt, the protoxide, or cobaltous oxide, CoO, which is the salifiable base of the metal, and the sesquioxide, Co_2O_3; these two oxides are capable of uniting with each other in different proportions. According to Schwarzenberg, an acid oxide, Co_3O_5, may be obtained, in combination, by strongly igniting the protoxide or the carbonate with potassic hydrate; a crystalline compound is thus formed, which when dried at 100° (212° F.), consists of $K_2O.3Co_3O_5.3OH$.

(805) **COBALTOUS OXIDE**, or *Protoxide of cobalt*; $CoO = 75$.—This oxide, when dried at a low temperature, is of a greenish-grey colour; when heated to dull redness in the air it absorbs oxygen and becomes black, forming an oxide, Co_3O_4, corresponding to the black or magnetic oxide of iron, but if more strongly heated it again loses oxygen, and becomes reconverted into the protoxide, which is of a brown colour, and which must be cooled in a current of carbonic anhydride to prevent its absorbing oxygen (Russell). Cobaltous oxide is soluble in acids, and forms solutions which, when concentrated, are of a beautiful blue colour,

but become pink on dilution. The oxide forms an important article of commerce, from its employment for the production of a blue colour in painting on porcelain. When describing the preparation of nickel, a process will be detailed which furnishes an oxide of cobalt fit for this purpose (818). Cobaltous oxide combines with bases as well as with acids. If fused with potassic hydrate it forms a blue compound, which is decomposed by water; when heated with magnesic nitrate, a pale pink residue, consisting of a combination of the magnesia with oxide of cobalt, is obtained; with alumina it forms the blue pigment known as Thénard's blue, and with zincic oxide the compound constitutes Rinman's green.

The *zaffre* of commerce is a very impure oxide of cobalt procured by imperfectly roasting cobalt ore, mingled with 2 or 3 times its weight of siliceous sand.

Smalt is a beautiful blue glass coloured by oxide of cobalt; it is chiefly manufactured in Saxony. It was at one time used largely by paper-stainers to produce a blue colour. In preparing smalt, the cobalt ore is first roasted; but the roasting is arrested at a particular stage, the object being to oxidize the cobalt, whilst the nickel, copper, and iron remain in combination with arsenic and sulphur; it is necessary to leave a sufficient amount of arsenic in the mass to retain these metals, as the admixture of a very small quantity of the oxides either of iron, nickel, or copper with the glass, seriously injures the purity of its colour.

From 4 to 5 parts of the roasted ore in powder are next mingled with 10 parts of ground calcined quartz and 4 parts of potassic carbonate, and the mixture is slowly melted in pots arranged in a furnace resembling that used in making ordinary glass. The oxide of cobalt combines with the fused potassic silicate; a deep blue glass is thus formed, whilst the mixed arsenides and sulphides of nickel, copper, and iron fuse, and collect at the bottom of the pot, in the form of a brittle mass, of metallic appearance, commonly known as *speiss*. The pot is then skimmed, and the glass is ladled out, and poured into cold water, by which means it is split into innumerable fragments: the speiss is cast into ingots and used in the manufacture of nickel. The broken glass is stamped to powder, and subsequently ground between granite stones, which are caused to revolve under water, in a vessel through which a gentle stream of water is continually flowing, which thus carries off with it the powdered smalt in suspension: it is made to pass through a number of depositing vessels, so arranged that the overflow from the first shall pass into the second, that from the second into the third, and so on: each of these vessels is successively larger than the one which precedes it, so that the period for which the washings are retained in each goes on progressively increasing, and the particles deposited increase progressively in the minuteness of their subdivision; the colour becoming less intense, the greater the degree of subdivision of its particles.

Another valuable pigment into the composition of which cobalt enters is of a pale blue colour, and is known as *Thénard's blue*. The most approved method

of preparing it consists in precipitating cobaltous nitrate by means of hydric dipotassic phosphate, and mixing the precipitate whilst still moist with four or five times its bulk of the gelatinous mass obtained by adding sodic carbonate to a dilute solution of alum perfectly free from iron. The mixture is dried and then exposed to a dull red heat in a covered crucible. The brilliancy of the colour is much impaired by the reducing action of the combustible gases of the fuel. The best preventive of this effect is found to consist in placing a little mercuric oxide at the bottom of each crucible; by the decomposition of this oxide an atmosphere of oxygen is obtained, and the metallic mercury is dissipated in vapour (Regnault, *Cours Elém. de Chimie*, vol. iii. p. 150).

Rinman's green is a pigment of analogous composition, containing oxide of cobalt combined with zincic oxide.

(806) **COBALTOUS HYDRATE**, or *Hydrated oxide of cobalt*, $CoH_2O_2 = 93$, is precipitated on the addition of a solution of potassic or sodic hydrate to a solution of any of its salts. The pale blue precipitate which is first formed is a basic cobaltous salt, but if an excess of alkali be used, it quickly becomes violet, and finally rose-coloured, which is the true colour of the hydrated oxide: these changes occur most rapidly if the liquid is warmed. It becomes of a dingy green if exposed to the air whilst moist, owing to the gradual absorption of oxygen. The hydrated protoxide is readily dissolved by a solution of ammonic sesquicarbonate, and also by excess of ammonia, especially in the presence of a neutral ammonium salt.

(807) **COBALTIC OXIDE**, or *Sesquioxide of cobalt*, $Co_2O_3 = 166$, may be prepared by suspending the hydrated protoxide of the metal in water, and passing a current of chlorine through the liquid; cobaltous chloride is formed and dissolved, whilst a black hydrated cobaltic oxide is precipitated, $Co_2H_6O_6$. The reaction may be thus expressed: $3(CoH_2O_2) + Cl_2 = Co_2H_6O_6 + CoCl_2$. If the cobaltous oxide be suspended in a solution of potassic hydrate instead of in pure water, the whole of the cobalt is converted into sesquioxide. It may be rendered anhydrous by a gentle heat, but at a higher temperature it becomes converted into a black oxide, Co_3O_4 or $CoO.Co_2O_3$, corresponding with the magnetic oxide of iron. This *cobaltoso-cobaltic oxide* is sometimes deposited in small, hard anhydrous, brilliant, steel-grey octahedra when a pure aqueous solution of roseocobaltic chloride (808) is boiled. In this form it is insoluble in nitric acid, hydrochloric acid, and aqua regia: it is but slowly attacked by heating it with oil of vitriol or with hydric potassic sulphate. The basic powers of the sesquioxide are extremely feeble. Cold sulphuric, nitric, hydrochloric, phosphoric, and acetic acids dissolve the hydrated oxide, but the salts are gradually converted into those of the protoxide at ordinary temperatures, and immediately if the solutions are heated.

(808) **AMMONIACAL COMPOUNDS OF COBALT.**—When a solution of a cobaltous salt in ammonia is exposed to the air, it absorbs oxygen rapidly, although the hydrated cobaltous oxide itself has only a slight tendency to do so. When the hydrated oxide is dissolved in a solution of ammonic chloride containing free ammonia, the absorption of oxygen proceeds quickly, and the liquid gradually acquires a violet-red colour. If, at this stage, it be supersaturated with hydrochloric acid in the cold, a heavy brick-red crystalline powder is precipitated, consisting of *roseocobaltic chloride*, $Co_2Cl_6.10NH_3.OH_2$.

It may be obtained in a pure state by mixing a solution of 5 grams of crystallized cobaltous chloride in 90 c. c. water with 27 c. c. of strong ammonia, and adding a solution of 2·5 grams of potassic permanganate in 100 c. c. water. After 24 hours the solution is filtered, neutralized with hydrochloric acid, and the salt precipitated by adding three vols. of hydrochloric acid, and one-third vol. of alcohol. The product thus obtained is quite free from *purpureocobaltic chloride*, $Co_2Cl_6.10NH_3$, but is immediately converted into the latter, when its solution is boiled with a trace of hydrochloric acid. The new salt is soluble in hot water slightly acidulated with hydrochloric acid, and as the liquid cools, beautiful ruby-red octahedral crystals are deposited (F. Claudet). This remarkable compound is quite insoluble in boiling strong hydrochloric acid, and may be employed as a means of obtaining chemically pure cobalt. When heated to redness it loses ammonia and ammonic chloride, leaving pure cobaltous chloride, which may be reduced to the metallic state by strongly heating it in a current of hydrogen gas. When digested with water and argentic oxide, its chlorine is exchanged for oxygen, and a red strongly alkaline liquid is produced, containing *purpureocobaltic oxide;* this unites with acids, and forms a peculiar class of salts: the alkaline solution emits no smell of ammonia.

Fremy, in an elaborate series of researches on the ammoniacal compounds of cobalt, has shown (*Ann. Chim. Phys.*, 1852, [3], xxxv. 257) that, independently of the compounds above described, and of the ammoniacal compounds obtained with the ordinary salts of the metal, three other sets of salts may be procured, which he regards as compounds of different oxides of cobalt with various proportions of ammonia: the first of these bases he names *oxycobalt*. Its salts crystallize readily; they have for the most part an olive colour, and may be dissolved in a solution of ammonia without change, but when placed in cold water they are decomposed with evolution of oxygen and deposition of a green basic salt; the salts of this base appear to contain a dioxide of cobalt, which, however, cannot be isolated. The second base, from the yellow colour of its salts, he terms *luteocobalt;* according to Mills, cobaltic chloride when heated with ammonic chloride, a large excess of ammonia, and a powerful oxidizing agent such as potassic permanganate, is almost entirely converted into the chloride of this base; the base itself has been isolated; it has a strongly alkaline reaction, and its salts crystallize easily. The third base is termed *fuscobalt;* it forms brown uncrystallizable salts, which, under the influence of ammonia and of acids, are converted into roseo- and luteocobaltic salts. Further details regarding the preparation of these different compounds are also contained in a paper by Gibbs and Genth (*Chem. Gaz.*, 1857, p. 141), who have described an additional series, to which they give the name of salts of *xanthocobalt*, from the brilliant yellow colour of these compounds. The *xanthocobaltic chloride*, $Co_2(NO_2)_2Cl_4.10NH_3$, may be obtained in crystals by decomposing the sulphate of this base with a solution of baric chloride; and the *sulphate*, $Co_2(NO_2)_2 2SO_4.10NH_3$, is easily prepared by passing a rapid current of nitrous acid through an ammoniacal solution of cobaltous sulphate, taking care to preserve the alkalinity of the liquid by the occasional addition of ammonia, or by exposing a mixture of cobaltous sulphate, potassic nitrite, and ammonia to the air. The solution gradually assumes a dark yellowish-brown colour, and if left to evaporate spontaneously, deposits the sulphate of the new base in the form of thin plates derived from the right rhombic prism. Salts of xanthocobalt are always formed when salts of purpureo- or roseocobalt are acted on by alkaline nitrites either in the cold or when heated.

A new class of salts, the *croceocobaltic salts*, are formed by the action of alkaline nitrites on ammoniacal solutions of cobalt under certain circumstances. When a solution of ammonic nitrite containing much free ammonia is added to a warm solution of cobaltous chloride and ammonic chloride, it absorbs oxygen,

and becomes of an orange colour, gradually depositing orange-brown crystals of *croceocobaltic nitrate*, $Co_2(NO_2)_4 2NO_3.8NH_3$; the chloride has the formula, $Co_2(NO_2)_4Cl_2.8NH_3$.

All the compounds of these bases are decomposed when boiled with a solution of potassic or sodic hydrate, hydrated cobaltic oxide being precipitated, whilst ammonia is expelled.

The following table will afford a general comparative view of these different classes of salts, including the double salts which ammonia forms with the protoxide of the metal; many of them have been further examined by Braun (*Ann. Chem. Pharm.*, 1864, cxxxii. 33, and 1867, cxlii. 50; also Gibbs, *Ann. Jour. Sci.*, [3], vi. 116, and viii. 189, 284); in all probability they are compounds of very complex constitution, formed on the ammonium type:

1. *Double Salts of Ammonia and Protoxide of Cobalt.*

Nitrate	...	$Co2NO_3.6NH_3.2OH_2$
Chloride	...	$CoCl_2.\ 6NH_3.3OH_2$.

2. *Salts of Oxycobalt.*

Nitrate	...	$CoO.2NO_3.5NH_3.OH_2$
Sulphate	...	$2[CoO.SO_4.5NH_3].3OH_2$.

3. *Salts of Luteocobalt.*

Nitrate	...	$Co_2 6NO_3.12NH_3$
Chloride	...	$Co_2Cl_6.\ 12NH_3$.

4. *Salts of Fuscobalt.*

Nitrate	...	$Co_2O_4NO_3.8NH_3.3OH_2$
Chloride	...	$Co_2OCl_4.\ 8NH_3.3OH_2$.

5. *Salts of Xanthocobalt.*

Nitrate	...	$Co_2(NO_2)_2 4NO_3.10NH_3$
Chloride	...	$Co_2(NO_2)_2Cl_4.\ 10NH_3$.

6. *Salts of Roseocobalt.*

Nitrate	...	$Co_2 6NO_3.10NH_3.2OH_2$
Chloride	...	$Co_2Cl_6.\ 10NH_3.OH_2$.

7. *Salts of Purpureocobalt.*

Acid-sulphate		$Co_2O_3\ 4SO_3.10NH_3.5OH_2$
Chloride	...	$Co_2Cl_6.\ 10NH_3$.

8. *Salts of Croceocobalt.*

Nitrate	...	$Co_2(NO_2)_4 2NO_3.8NH_3$
Chloride	...	$Co_2(NO_2)_4Cl_2.\ 8NH_3$.

(809) **SULPHIDES OF COBALT.**—Three sulphides of this metal exist,—a protosulphide, CoS; a sesquisulphide, Co_2S_3; and a disulphide, CoS_2. The latter may be prepared by heating cobaltous carbonate with sulphur, not allowing the temperature to rise too high. The most important of these is the *protosulphide*, which is obtained in a hydrated condition by precipitating a solution of cobaltous acetate by sulphuretted hydrogen, or by mixing any neutral solution of a cobaltous salt with ammonic hydric

sulphide. In this form it absorbs oxygen rapidly from the air, and becomes converted into cobaltous sulphate. If a mixture of cobaltous oxide and potassic persulphide (liver of sulphur) be fused in a covered crucible, fused sulphide of cobalt is obtained at the bottom of the crucible. The *sesquisulphide*, which is occasionally met with in octahedra of a grey colour, may be obtained by heating cobaltic oxide at about 260° (500° F.), in a current of sulphuretted hydrogen.

(810) **COBALTOUS SULPHATE**, or *Sulphate of cobalt*, $CoSO_4.7OH_2 = 155 + 126$, (*Density, anhydrous*, 3·531), is isomorphous with magnesic sulphate. The anhydrous salt contains 38·06 of metallic cobalt, or 48·39 of the protoxide.

(811) **COBALTOUS NITRATE**, or *Nitrate of cobalt*, $Co_2NO_3.6OH_2 = 183 + 108$, (*Density*, 1·83), is prepared by dissolving the oxide in nitric acid. It is a deliquescent salt, which is sometimes employed as a reagent for the blowpipe: a fragment of the compound under examination is supported either upon charcoal, or upon a bent platinum wire, and moistened with a minute quantity of a strong solution of the cobaltous nitrate. When treated in this way, many of the compounds of magnesium yield a pale pink-coloured mass after ignition, those of zinc give a green residue, and those of aluminium a blue.

(812) **Cobalt Yellow.**—If a concentrated solution of potassic nitrite be gradually added to a solution of cobaltous nitrate acidulated with nitric or acetic acid, a beautiful orange-yellow compound is precipitated in microscopic four-sided prisms with pyramidal summits: it is sparingly soluble. According to A. Stromeyer, it consists of $Co_2O_3.2N_2O_3.6KNO_3.2OH_2$, and contains 13·6 per cent. of metallic cobalt. Erdman (*Jour. pr. Chem.*, 1866, xcvii. 385) and Sadtler (*Ann. Jour. Sci.*, [2], xlix. 189) have shown, however, that the composition of the precipitate varies according to circumstances. When excess of potassic nitrite is added to a neutral solution of cobaltous chloride, a yellow crystalline precipitate of the composition of *potassic cobaltous nitrite*, $CoK_2(NO_2)_4.OH_2$, is produced; whilst if the solution of potassic nitrite is dilute, and the cobalt solution maintained in excess, a black or green crystalline precipitate of *potassic dicobaltous nitrite*, $Co_2K_2(NO_2)_6.OH_2$, is formed. On the contrary, when the solution is strongly acid with acetic acid, *tripotassic cobaltic nitrite*, $Co_2K_6(NO_2)_{12}$, is thrown down, either anhydrous or with 1, 2, 3, or 4 mols. of water of hydration, according to the state of concentration of the solution. With sodic nitrite, in solutions acid with acetic acid, *tetrasodic cobaltic nitrite*, $Co_2Na_4(NO_2)_{10}.OH_2$, and *trisodic cobaltic nitrite*, $Co_2Na_6(NO_2)_{12}.OH_2$, are formed. Minute quantities of cobalt in admixture with nickel may be discovered by its means, unless lime or other alkaline earths be present, for alkaline nitrites form compounds with nickel and the alkaline earths very closely resembling cobalt yellow in appearance: the calcium compound has the formula $K_2CaNi(NO_2)_6$.

(813) **COBALTOUS CARBONATES.**—Cobalt resembles magnesium, zinc, nickel, and copper, in the circumstance that when

solutions of its normal salts are mixed with a solution of sodic or potassic carbonate, the precipitate which falls is not a normal carbonate, but a mixture of normal carbonate with hydrated cobaltous oxide. If the two solutions be mixed when hot, the red precipitate is said to have the formula $5CoO.2CO_2.4OH_2$. If the salts be mixed at the ordinary temperature, the precipitate is of a brighter red, and has the composition $4CoO.2CO_2.5OH_2$. If either of these precipitates be boiled with an excess of sodic carbonate, it assumes an indigo-blue colour, and is converted into the compound $4CoO.CO_2.4OH_2$; this absorbs oxygen and becomes green during washing. The true normal carbonate, $3CoCO_3.2OH_2$, is formed by digesting either of the basic cobaltous carbonates with the so-called bicarbonate of sodium or ammonium.

A hydrated *tricobaltous arseniate*, $Co_32AsO_4.8OH_2$, is found native in minute crystals, and is known as *cobalt bloom*.

(814) **Characters of the Salts of Cobalt.**—The crystallized cobaltous salts are red; when anhydrous they are usually lilac-coloured. Their solutions are blue when in a very concentrated form; at a particular stage of dilution they are red when cold, but become blue on heating, the red colour returning as the liquid cools; when mixed with a larger proportion of water they exhibit a delicate rose colour, and this tint is perceptible even when the solution is very much diluted. They have an astringent metallic taste.

Before the blowpipe the compounds of cobalt are easily recognized by the intense blue colour which they communicate to a bead of borax in the oxidizing flame.

In solution, the salts which this metal forms with the mineral acids give no precipitate with *sulphuretted hydrogen*, if the liquid be slightly acidulated with sulphuric or hydrochloric acid; but the cobalt is completely precipitated by it from a dilute neutral solution of the acetate. With *hydric ammonic sulphide* they yield a black sulphide. *Potassic carbonate* gives a rose-coloured basic carbonate, which is soluble in ammonic sesquicarbonate. *Potassic hydrate* precipitates a blue basic salt, which with excess of alkali becomes rose-coloured. *Ammonia* produces a similar effect, but readily redissolves the precipitate, forming a brownish solution which absorbs oxygen rapidly from the air, and acquires a red colour (808). The soluble *oxalates* give a sparingly soluble pink cobaltous oxalate, soluble in nitric acid and in ammonia. *Potassic ferrocyanide* gives a dirty green, and *potassic ferricyanide* a bulky reddish-brown precipitate; the latter reaction occurs even in ammoniacal solutions. On dissolving a few crystals of

sodic pyrophosphate in a solution of a cobaltous salt and adding *sodic hypochlorite* to the *cold* liquid, a deep brown-coloured solution of cobaltic phosphate is produced: nickel under the same circumstances forms a colourlesss liquid. Care must be taken not to warm the solution, as otherwise both metals would give a precipitate of the black hydrated peroxide.

(815) **Estimation of Cobalt.**—Cobalt is often estimated in the metallic form. Supposing that no compound of any other metal susceptible of precipitation by sulphuretted hydrogen be present, the solution is to be neutralized by means of potassic carbonate, mixed with a solution of potassic acetate, and the cobalt precipitated as sulphide by a current of sulphuretted hydrogen, the precipitate allowed to settle in a beaker closed by a glass plate, then collected on a filter and washed. The alkalies are prevented from effecting the complete precipitation of cobalt, as well as of iron, nickel, copper, and many other metals, by the presence of certain kinds of organic matter, such as that derived from the paper of the filter; special precautions are therefore required to avoid this accident. For this purpose the neck of the funnel with the filter and its contents is introduced into a small flask, a hole is made with a glass rod in the bottom of the filter, and the precipitate is washed into the flask; the filter after being moistened with concentrated nitric acid, is again washed; it is then dried, burnt, and the ash added to the contents of the flask, which are now boiled with nitric acid until the cobaltous sulphide is dissolved. The liquid so obtained is diluted and poured off from any particles of undissolved sulphur, evaporated to dryness, then mixed with sulphuric acid to convert the cobalt into sulphate, and the excess of acid expelled by a moderate heat. 100 parts of cobaltous sulphate indicate 38·06 of the metal. After the sulphide has been brought into solution by the nitric acid, the cobalt may also be precipitated in the form of hydrated oxide by an excess of pure potassic hydrate; the oxide is then thoroughly washed with boiling water, dried, ignited, and weighed: the black oxide thus obtained consists of Co_3O_4, and 100 parts correspond to 73 44 of metallic cobalt. Some chemists, however, prefer to reduce this oxide by heating it in a weighed tube, in a current of dry and pure hydrogen; but the process is not to be recommended, as, if after the operation the tube be weighed full of hydrogen, the weight is too little, and if the hydrogen be displaced by atmospheric air, the finely divided metal is apt to become partially oxidized.

(816) **Separation of Cobalt from the Metals of the Alkalies**

and Alkaline Earths, and from Aluminium.—This is readily effected by converting the cobalt into acetate, and passing sulphuretted hydrogen, as has been already mentioned in the preceding paragraph. Another plan consists in the addition of ammonic hydric sulphide to the solution previously neutralized by ammonia. If alumina be present, it will accompany the cobalt, but if this precipitate be redissolved in acid, and again thrown down by means of potassic hydrate in excess, the alumina will be retained; the cobaltous oxide is, however, apt to carry down traces of alumina; these may be removed by treating the precipitated oxide with a mixture of ammonia and ammonic chloride, which dissolves the cobalt, but leaves any traces of alumina which may have accompanied it. The cobalt is again precipitated by ammonic hydric sulphide.

(817) Separation of Cobalt from Zinc.—This is not easy. One of the best methods consists in precipitating the two metals together in the form of sulphides, dissolving this precipitate in nitric acid, and then adding an excess of potassic carbonate, and evaporating to dryness. After the mixed carbonates of zinc and cobalt have been well washed, they are heated in a bulb-tube in a current of dry hydrochloric acid; in this process carbonic anhydride is expelled, and the metals are converted into chlorides, whilst water is formed. The open end of the tube is in this case bent downwards at a right angle, and the aperture is made to dip into a small quantity of water contained in a flask: the zincic chloride, which is volatile, is carried forward in the current of gas; a portion of it is condensed in the bend of the tube, and the remainder is dissolved in the water placed for its reception. Cobaltous chloride alone remains in the bulb. The portion of the tube in which the zincic chloride has been condensed is cut off when the operation is complete, and is allowed to fall into the flask. The zinc and the cobalt are then easily determined separately by the usual methods.

Another method, when the metals are in solution as sulphates, consists in boiling the solution with binoxide of lead in excess; this precipitates all the cobalt, and, after removal of the trace of dissolved lead by sulphuretted hydrogen, the zinc may be determined in the usual way: if any nickel is present it will be found in the solution. The precipitate is boiled with alcohol and hydrochloric acid, filtered from the plumbic sulphate and chloride, and the solution treated with sulphuretted hydrogen, to throw down the lead: the cobalt is then determined in the usual way.

§ II. NICKEL: Ni″ = 59.

(818) **NICKEL**; *Density*, 8·28 to 8·66.—The peculiar characters of this metal were first recognised in 1751 by Cronstedt: it has a remarkable analogy with cobalt, and is always associated with it in nature, both as a constituent of meteoric iron, and in its ores, which present a composition similar to those of cobalt. It is most abundant in the form of kupfernickel (arsenide of nickel), and is extracted either from this ore or from *speiss*, which is an impure arseniosulphide of nickel, formed during the manufacture of smalt (805).

Preparation.—As the metal itself is now extensively used in alloys, of which German silver is one of the most important, great pains have been taken to procure it in a state of comparative purity, and several processes have been proposed for this purpose.

1.—According to Louyet, the method by which nickel is extracted from speiss at Birmingham on the large scale is as follows:—The speiss is first fused with chalk and fluor-spar, the metalliferous mass so obtained is reduced to powder, and roasted for twelve hours to expel the arsenic; the residue is next dissolved in hydrochloric acid, diluted with water, and the iron converted into a ferric salt by the cautious addition of bleaching powder. Milk of lime is then carefully added so long as ferric oxide falls, which carries down with it the last portions of arsenic: this precipitate is well washed, and the liquid, which retains all the cobalt and nickel, is treated with a current of sulphuretted hydrogen; the sulphides of copper, bismuth, and lead, are thus precipitated, and are thoroughly washed. All the nickel and cobalt still remain in the liquid; this liquid is boiled to expel sulphuretted hydrogen, neutralized with lime, and again treated with chloride of lime: the whole of the cobalt is thus thrown down as sesquioxide; after which the whole of the nickel is separated from the solution in the form of hydrated protoxide by adding milk of lime so long as any precipitate is produced. For further information on the technical production of nickel and cobalt we must refer our readers to Hofmann's *Bericht über die Entwickelung der Chemischen Industrie*, ii. p. 859.

2.—Nickel may be obtained pure upon a small scale, by dissolving the roasted ore in aqua regia, evaporating to expel the excess of acid, redissolving in water, and passing a current of sulphuretted hydrogen. The filtered liquid is

boiled with nitric acid, to convert the iron into a ferric salt; the solution is precipitated by an excess of caustic ammonia, filtered from the ferric oxide, and to the blue liquid potassic hydrate is added until the blue tint nearly disappears; a pale green precipitate, consisting of hydrated nickel oxide and potash, is thus obtained, which must be well washed with hot water to remove the potash, and then reduced by ignition in a current of hydrogen gas: when obtained in this manner it is generally pyrophoric. If heated for an hour at a blacksmith's forge, in a crucible lined with charcoal, a well-fused button of carbide of nickel is produced. A button of the pure metal may however be procured by heating nickel oxalate intensely in a crucible with a luted cover, without any other reducing agent than the carbonic oxide furnished by its own decomposition.

3.—It may also be obtained in laminæ by the electrolysis of a solution of the ammonic nickel sulphate, $NiSO_4.(NH_4)_2SO_4.6OH_2$.

Properties.—Pure nickel is a brilliant, silver-white, hard, but ductile metal, somewhat more fusible than iron, which, according to Deville, it even surpasses in tenacity. At ordinary temperatures it is susceptible of magnetism, but it loses this property almost entirely if heated to a point exceeding 330° (626° F.), although it recovers its magnetic power on cooling. Nickel becomes oxidized by exposure to a current of air at a high temperature. The metal, if suspended in water, is easily attacked at ordinary temperatures by chlorine or bromine. It is also readily dissolved by nitric acid and by aqua regia, and slowly by dilute sulphuric or hydrochloric acid with evolution of hydrogen. Owing to the remarkable power which nickel possesses of rendering brass white, it is now much used in the manufacture of *packfong*, or German silver, a compound of zinc, nickel, and copper, in which the proportions of the metals may vary considerably. A good alloy consists of 5 equivalents of copper, 3 of zinc, and 2 of nickel, or, in 100 parts, of 51 of copper, 30·6 of zinc, and 18·4 of nickel: according to Christofle and Bouilhet, German silver containing 15 per cent. of nickel is remarkable for its malleability, homogeneity, and whiteness, and is capable of being drawn into wires or rolled into sheets of any thickness. Packfong is of a yellowish-white colour, and when freshly polished closely resembles silver in appearance. *Tutenag* is the name given by the Chinese to a similar alloy, consisting of 8 parts of copper, 6½ of zinc, and 3 of nickel.

The native arsenides of nickel are important, as they form the principal ores of the metal. *Kupfernickel,* Ni_2As_2, is a true nickel arsenide; it contains 44·03 parts of nickel to 55·97 of arsenicum; part of the arsenicum in this ore is sometimes displaced by an equivalent amount of antimony. It has a reddish colour and a metallic lustre. It is not attacked by hydrochloric acid, but is soluble in nitric acid, and is decomposed when heated in the air or in a current of chlorine. *Arsenical nickel,* $NiAs_2$, is another

native compound of the two metals: by ignition in closed vessels it loses half its arsenicum, and becomes converted into kupfernickel. A compound of nickel with arsenicum and sulphur, corresponding to mispickel, and known as *nickel glance*, NiSAs, is also found native.

A *phosphide of nickel*, Ni_4P_2, has been obtained by Schenk as a black powder on pouring a solution of nickelous chloride into a boiling mixture of phosphorus with potassic hydrate solution.

(819) **NICKELOUS CHLORIDE**, or *Chloride of nickel*, $NiCl_2 = 130$, is formed by dissolving the oxide in hydrochloric acid. Its solution, on evaporation, yields green hydrated crystals with $9OH_2$; by heat it may be obtained as a yellowish-brown anhydrous mass, which is volatile at a high temperature, and condenses in yellow crystalline scales, which are slowly dissolved by boiling water. If heated in a current of air, a portion of the chlorine is expelled, and a corresponding quantity of nickelous oxide is formed.

(820) **OXIDES OF NICKEL.**—Nickel forms two oxides; a protoxide, NiO, and sesquioxide, Ni_2O_3. Only the first oxide forms salts.

Nickelous Oxide, or *Protoxide of nickel*; $NiO = 75$; *Density*, 5·75; *Comp. in* 100 *parts*, Ni, 78·67; O, 21·33.—This oxide may be obtained in the anhydrous form by igniting the nitrate or carbonate of the metal in a covered crucible, when it is left of an olive-green colour. It may be precipitated from its salts by potassic hydrate, as a bulky light-green hydrate (NiH_2O_2?), and may be obtained crystallized by decomposing the solution of nickel carbonate in ammonia by ebullition. Nickelous oxide is readily soluble in acids, forming salts which have a pale green colour. It yields insoluble compounds with potash and with soda, which, however, may be decomposed by frequent washings with boiling water. It also forms insoluble compounds with baryta, strontia, and several other bases; ammonia dissolves it, forming a deep blue solution. A solution of ammonic chloride also dissolves it slowly.

Sesquioxide of Nickel, $Ni_2O_3 = 166$.—This is a black powder which may be obtained as a hydrate, $Ni_2H_6O_6$, by treating the hydrated protoxide with a solution of sodic hypochlorite. It does not combine with acids, and gives off a portion of its oxygen by ignition, or by heating it with nitric or sulphuric acid, which forms with it salts of the protoxide.

(821) **SULPHIDES OF NICKEL.**—Three of these compounds are known; a subsulphide, a protosulphide, and a disul-

phide. The *protosulphide*, NiS=91, occurs native as *millerite* in greyish or yellowish capillary crystals, which are insoluble in hydrochloric, but soluble in nitric acid: it may be formed artificially by fusing sulphur with nickel. It may also be obtained by fusing a persulphide of one of the alkali-metals with diarsenide of nickel, when it is left in yellow crystalline scales. A black hydrate of this sulphide is produced when a salt of nickel is precipitated by ammonic hydric sulphide; in this form it absorbs oxygen from the air, and is gradually converted into nickel sulphate. The *subsulphide*, Ni_2S, may be formed by reducing nickel sulphate by means either of charcoal or of hydrogen gas. The *disulphide*, NiS_2, is left as a steel-grey powder on treating with water the mass obtained by heating to redness an intimate mixture of nickel carbonate, potassic carbonate, and sulphur.

(822) **NICKELOUS SULPHATE**, or *Sulphate of nickel*; $NiSO_4.7OH_2$=155+126.—This salt may be obtained by dissolving pure metallic nickel, or its oxide or carbonate, in sulphuric acid: it may also be prepared from commercial nickel by dissolving it in aqua regia, evaporating to dryness, then redissolving in water, and after filtering from any arsenate of iron which may be present, precipitating the copper with metallic iron. The iron in solution is peroxidized by nitric acid, and after adding sulphuric acid and evaporating to dryness, the product is dissolved in water. This solution contains only nickelous and ferric sulphates, from which the iron may be precipitated by pure baric carbonate. Nickelous sulphate crystallizes in green rhombic prisms, which require 3 parts of cold water for solution, but are insoluble in alcohol: the prismatic crystals, when exposed to light, are converted into small regular octahedra, aggregated together in the form of the original crystal, which becomes opaque. It may be obtained in octahedra at once with $6OH_2$ (density, 2·037), by crystallizing at a temperature between 15° and 25° (59° and 77° F.).

A potassic nickelous sulphate ($NiSO_4.K_2SO_4.6OH_2$; *density, anhydrous*, 2·897, *cryst.* 2·190) may be formed by adding potassic hydrate to the impure solution of speiss, and by repeated crystallizations may be freed from all impurities except traces of iron and cobalt: it was at one time used as a means of purifying nickel for commercial purposes. Other double sulphates of nickel may be obtained. Each molecule of nickel sulphate in the solid form absorbs 6 molecules of ammoniacal gas. An insoluble *basic sulphate* is obtained by adding to a solution of the normal sulphate a quantity of potassic hydrate insufficient for its complete decomposition.

(823) **NICKELOUS NITRATE**, *Nitrate of nickel*; $Ni2NO_3.6OH_2$.—The normal salt crystallizes in emerald green prisms, which are soluble in about twice their weight of cold water; when heated it forms a basic salt.

(824) **NICKEL CARBONATES.**—There are several basic nickelous carbonates, of a green colour. The normal carbonate is precipitated as a crystalline powder, when a solution of nickel nitrate is poured into a large excess of a solution of hydric sodic carbonate (bicarbonate of soda).

(825) **Characters of the Salts of Nickel.**—The salts of this metal are of a delicate green colour, both when in the solid state and when in solution; they redden litmus feebly. They have a sweet astringent metallic taste, and when taken internally excite vomiting.

Before the blowpipe, in the oxidizing flame, the salts of nickel give a reddish-yellow glass with borax, which becomes much paler as it cools. The addition of a potassium salt colours the bead blue. In the reducing flame, greyish particles of reduced nickel are disseminated through the bead.

In solution, *sulphuretted hydrogen* gives no precipitate if the liquid be acidulated with sulphuric acid; but it precipitates a dilute nearly neutral solution of nickel acetate very perfectly when aided by a gentle heat. *Hydric ammonic sulphide* gives a black sulphide slightly soluble in excess of the precipitant, forming a dark-brown solution. *Ammonia* gives a pale green precipitate, soluble in excess of ammonia, forming a bright blue solution, from which an excess of potassic hydrate precipitates a green compound of nickelous oxide and potash. *Potassic* and *sodic hydrates* throw down a pale-green, bulky, hydrated nickelous oxide, insoluble in excess of the alkali. The *carbonates of the alkali-metals* give a pale apple-green precipitate of basic nickelous carbonate, which is readily soluble in ammonic sesquicarbonate. *Potassic ferrocyanide* gives a greenish white, and *potassic ferricyanide* a yellowish-green precipitate, both of which are soluble in hydrochloric acid. *Hydric potassic oxalate* in a neutral solution, if not too dilute, causes the deposition of a greenish-white, sparingly soluble nickelous potassic oxalate soluble in excess of ammonia. When mixed with *sodic acetate* and *hypochlorite* and boiled, a solution of a nickelous salt deposits a deep blue, almost black, coating of the peroxide on the sides of the vessel.

(826) **Estimation of Nickel.**—Nickel is best estimated in the form of protoxide, which, when precipitated by means of potassic hydrate, requires careful and long continued washing with hot water to remove the adhering alkali: 100 parts of nickelous oxide contain 78·67 of the metal.

(827) **Separation of Nickel from the Alkalies and Earths and from Zinc.**—For this purpose the same processes as those adopted for the separation of cobalt (816) may be employed.

(828) **Separation from Cobalt.**—The following method, devised by Liebig and slightly modified by Hadow, answers this purpose exceedingly well. The nitric solution of the cobalt and nickel, having been freed from all other metals except potassium and sodium, is nearly neutralized with potassic carbonate, and then mixed with an excess of hydrocyanic acid, and with pure potassic hydrate, after which the mixture is left exposed to the air in a shallow open dish for a few hours. During this time oxygen is absorbed, and the liquid acquires a pale yellow colour. A tripotassic cobalticyanide, K_3CoCy_6, is formed, and a nickelous potassic cyanide, $2KCy.NiCy_2$, is produced at the same time. The formation of the cobalticyanide may be traced as follow: cobaltous cyanide is first formed; $2HCy + CoO = CoCy_2 + OH_2$, and this cyanide, by exposure to air with an excess of potassic cyanide and hydrocyanic acid, yields tripotassic cobalticyanide, whilst oxygen is absorbed and water is separated; $4CoCy_2 + 12KCy + 4HCy + O_2 = 4K_3CoCy_6 + 2OH_2$. The nickelous potassic cyanide is very simply formed; for no compound corresponding to the cobalticyanide is obtained with nickel; $4KCy + NiO + OH_2 = 2KCy.NiCy_2 + 2KHO$. If the strongly alkaline solution be now boiled, and a solution of mercuric nitrate be added in slight excess, so as to produce a precipitate which, from its yellowish colour, shows that the mercuric oxide is in excess, the nickel salt is decomposed, hydrated nickelous oxide is precipitated, and mercuric cyanide is produced; $2KCy.NiCy_2 + HgO + OH_2 = 2KCy.HgCy_2 + NiH_2O_2$.

Potassic cobalticyanide is not decomposed by mercuric oxide, but remains in solution, and may be filtered from the nickelous oxide, which requires to be carefully ignited in a platinum crucible until it ceases to lose weight. After cautiously neutralizing the filtrate with nitric acid, the cobalt may then, by the addition of a solution of mercurous nitrate, be precipitated as a white mercurous cobalticyanide: the precipitate is collected, dried, and ignited in a porcelain crucible, when pure cobaltous oxide is left.

If, instead of precipitating the mixed cyanides by means of mercury, a solution of chloride of soda be added in excess to the boiling alkaline liquid, in quantity sufficient to destroy the free potassic cyanide, the nickel is precipitated as an intensely black sesquioxide; in this form it may be readily washed, and then converted into the protoxide by ignition, in which state it may be weighed. Traces of nickel which escape discovery by other methods may thus often be detected in cobalt. Care must be

taken to ascertain the absence of manganese, as it would go down with the nickel, accompanied by traces of iron, if the latter metal were present.

Cobalt may also be separated from nickel by precipitation with potassic nitrite in excess, provided no other metals but nickel, manganese, or zinc are present; the operation requires care, however, and attention to details which are given in works specially devoted to quantitative analyses.

§ III. URANIUM: U=120.

(829) **URANIUM**; *Density*, 18·4.—The compounds of this metal are but sparingly distributed over the surface of the earth. It was originally discovered by Klaproth, in *pitchblende*, which contains from 40 to 90 per cent. of the green uranium oxide, $UO.U_2O_3$; the remainder of the mass consists of variable quantities of copper, lead, iron, arsenicum, and frequently of cobalt and nickel. It is found in large quantity in Joachimsthal in Bohemia. *Uranite*, which is a mineral of micaceous structure, of rarer occurrence, consists of a hydrated calcic diuranic diphosphate, $Ca''_2(U_2O_2)''_2P_2O_8.8OH_2$. *Chalcolite*, $Cu''_2(U_2O_2)''_2P_2O_8.8OH_2$, is a similar mineral, in which copper takes the place of calcium. *Autunite*, found near Autun, also in Cornwall, has the composition $U_2O_3.CaO.P_2O_5.10OH_2$.

In order to extract uranium from pitchblende, the mineral is heated to redness, and thrown into water, which renders it capable of being readily pulverized: Ebelmen then treats the ore in the following manner:—The fine powder is washed with dilute hydrochloric acid, heated with charcoal, and digested in strong hydrochloric acid, by which the earthy matters and most of the iron, arsenic, and sulphur are removed: the washed residue is roasted and then treated with nitric acid; the solution thus obtained is evaporated nearly to dryness, to expel the excess of acid, and is diluted, by which means most of the ferric arsenate is precipitated. Sulphuretted hydrogen is then passed through the clear solution, and the liquid is filtered from the sulphides of copper, lead, and arsenic thus thrown down; after which it is again evaporated until crystals of uranic nitrate begin to be formed. This salt is decomposed by heating it to redness, and the uranium oxide which is left is mingled with charcoal and heated in a glass tube through which a current of dry chlorine is passing; carbonic anhydride and carbonic oxide are thus formed, and a volatile green uranous chloride, UCl_2, sublimes. This chloride, when heated with potassium in a platinum crucible, yields potassic chloride and metallic uranium: intense heat is evolved during the reaction of the potassium on the uranous chloride, and the resulting metal is partially fused. By placing layers of sodium, potassic chloride, and a mixture of potassic and uranous chlorides, in a porcelain crucible contained within an earthen one lined with charcoal, and then gradually heating it in a blast furnace, the metal may be obtained in fused globules. The isolation of metallic uranium is due to Péligot (*Ann. Chim. Phys.*, 1842, [3], v. 5), the substance originally supposed to be the metal having been proved by him to be its protoxide.

Uranium as thus obtained is of a steel-white colour: it appears to be slightly malleable; it is not oxidized by exposure to air or to water at the ordinary temperature: but if heated in the air it burns brilliantly: sulphuric and hydrochloric acids dissolve it with evolution of hydrogen. In its chemical relations it is somewhat analogous to iron and manganese.

(830) **URANIUM CHLORIDES.**—Uranium forms three chlorides, U_2Cl_5, U_4Cl_6, and UCl_2, besides an oxychloride, $U_2O_2Cl_2$.

Uranic Chloride, U_2Cl_5, is formed together with uranous chloride when excess of dry chlorine is passed over a moderately heated mixture of charcoal with any of the oxides of uranium, or with uranic oxychloride, $U_2O_2Cl_2$. It occurs in two forms, as a light brown powder, when the current of gas is rapid, and as long dark needles when it is slow: these are of a splendid red by transmitted light, and brilliant metallic green by reflected light. The uranous chloride which is always formed at the same time is deposited in magnificent octahedral crystals in that part of the tube nearest the heated mixture, the uranic chloride being condensed in the cool part of the tube. The uranic chloride is readily decomposed by heat, yielding uranous chloride with evolution of chlorine. When it is heated in a current of dry ammonia a black *uranium nitride* is produced (Roscoe, *Jour. Chem. Soc.*, 1874, xxvii. 933).

Uranous Chloride, or the *dichloride*, UCl_2 (Péligot's protochloride), is a volatile, deliquescent compound, crystallizing in dark-green octahedrons which have a metallic lustre, and are decomposed when boiled with water; the method of preparing it has just been described (829). If dry hydrogen be passed over uranous chloride, heated to redness in a glass tube, the *sesquichloride*, U_4Cl_6, is produced; it crystallizes in slender dark-brown needles, which are but slightly volatile; they are very soluble in water and form a deep purple solution, from which ammonia throws down a brown suboxide; this oxide rapidly absorbs oxygen from the air. The corresponding *bromides* have been examined; they closely resemble the chlorides.

(831) **URANIUM OXYCHLORIDE,** $U_2O_2Cl_2$.—Péligot's *chloride of uranyl* is an *oxychloride*, $U_2O_2Cl_2$, or $U_2O_3.UCl_3$, somewhat analogous to chlorochromic acid (895), formed by passing chlorine over uranous oxide: it is deliquescent, and forms a yellow solution with water; with the chlorides of the alkali-metals it yields remarkable double salts; the double salts with potassic chloride consists of $2KCl.U_2O_2Cl_2\,2OH_2$, and crystallizes in rhombic tables of a greenish-yellow colour.

(832) **URANIUM OXIDES.**—Uranium forms two principal oxides, a *protoxide*, or *uranous oxide*, UO, and a *sesquioxide*, or *uranic oxide*, U_2O_3; besides these a suboxide (U_4O_3?) and a peroxide appear to exist: two intermediate oxides may also be obtained, the *black oxide*, $2UO.U_2O_3$, and the *green oxide*, $UO.U_2O_3$.

Uranous Oxide, or the *protoxide*, UO = 136, may be obtained in several ways: one of the easiest consists in igniting uranic oxalate in closed vessels, or in a current of hydrogen, or by igniting potassic uranic chloride, or by heating it in hydrogen. In its anhydrous state the dilute acids are without action upon it, but its hydrate, which may be obtained in reddish-brown flocculi, by

adding ammonia to a solution of uranous chloride, UCl_2, is readily soluble in the acids: it forms green crystallizable salts, which have a strong tendency to absorb oxygen.

The **Black Oxide**, $2UO.U_2O_3$, may be prepared by heating the protoxide to bright redness, and suddenly cooling it, or by igniting uranic nitrate. It furnishes a pure and intense black, highly prized for colouring porcelain.

Uranoso-uranic Oxide, or the *green oxide* ($UO.U_2O_3$; *Density*, 7·31), which corresponds in composition to the magnetic oxide of iron, forms the principal constituent of pitchblende, and is prepared by heating the black oxide moderately in a current of oxygen or in the open air; by more intense ignition it becomes re-converted into the black oxide, and is again partially oxidized as it cools. It is soluble in hot concentrated sulphuric acid, but does not form distinct salts.

Uranic Oxide, or the *sesquioxide*, U_2O_3, partakes of the characters both of an acid and of a base. It is with difficulty obtained in a pure state. By exposing a solution of uranic oxalate to the sun's rays, a brownish-violet powder, which is a hydrate of the green oxide, $U_3O_4.3OH_2$, is deposited, whilst carbonic anhydride makes its escape: this precipitate absorbs oxygen on exposure to the air, and becomes converted into a greenish-yellow mass, which, according to Ebelmen, is a hydrated sesquioxide, $U_2O_3.2OH_2$. The sesquioxide may be obtained in the anhydrous state as a brick-red powder, by heating this hydrate to a temperature not exceeding 300° (572° F.). Uranic oxide reacts readily with acids, and forms salts of a bright yellow colour. Péligot found that the oxide, UO, evinced a strong tendency to unite with elementary bodies like a metal, and hence he proposed to call it *uranyl*, and explained the fact that the normal uranic salts are all formed by the action of uranic oxide upon two molecules of a monobasic acid instead of on six molecules. *Uranic nitrate*, for instance, which furnishes long lemon-yellow striated prisms, belonging to the trimetric system, consists, even when crystallized from a strongly acid solution, of $(U_2O_2)''2NO_3.6OH_2$. The crystals are very soluble in water, and also in alcohol and ether. Normal *uranic sulphate*, $U_2O_2SO_4$, is obtained in anhydrous amber-yellow crystals on evaporating a solution of the oxide in sulphuric acid. Numerous uranic double salts have also been formed; *uranic potassic sulphate* consists of $K_2(U_2O_2)''2SO_4.2OH_2$. If an attempt be made to prepare uranic oxide by decomposing the solutions of these salts by the addition of an alkali, an insoluble yellow precipitate, consisting of a compound of the

sesquioxide with the alkali, frequently called a *uranate* of the base, falls; potassic uranate has the formula, $K_2O.2U_2O_3.3OH_2$, and the other similar compounds have a corresponding composition; this compound cannot be decomposed even by boiling water.

'Uranium yellow' is a uranate of soda which is now prepared on a large scale by a process first indicated by Patera. The finely powdered ore (*pitchblende*) is roasted to remove sulphur and arsenic, and is then heated with 15 per cent. of soda-ash and 2 of nitre until it assumes a yellowish-brown colour. The product is next well washed with hot water and treated with the requisite quantity of sulphuric acid, which dissolves not only all the uranium, but also the copper, iron, manganese, nickel, cobalt, &c., originally present in the ore. On supersaturating with soda-ash these metals are precipitated whilst the carbonate of sodio-uranium remains in solution if a sufficient excess of soda has been taken. The clear golden yellow solution, after being boiled to decompose any bicarbonate which may be present, is exactly neutralized with sulphuric acid and boiled, when the 'uranium yellow' is thrown down in a finely divided state; it merely requires to be washed to be ready for the market. A uranium yellow sometimes occurs in commerce which is a hydrate retaining about 2 per cent. of ammonia, from which heat expels the water and ammonia, and also converts the sesquioxide into the black or the green oxide. The compounds of uranic oxide with the earths, however, stand a strong heat without decomposition, and are employed to communicate a beautiful and peculiar fluorescent yellow to glass.

Fairley (*Chem. News*, 1875; xxxii. 219) states that on mixing solutions of uranic nitrate and hydric peroxide, a yellowish-white precipitate is produced, whose composition is represented by the empirical formula, UH_2O_3; he regards it as a compound of uranic oxide, U_2O_3, with a higher oxide, UO_3.

(833) **Characters of the Uranium Compounds.**—1. The *uranous salts* are of a green colour, and have a strong tendency to form double salts with salts of the alkali-metals which contain the same acid as themselves. In solutions of the uranous salts, *ammonia* and the *alkalies* give a gelatinous, blackish-brown precipitate of hydrated uranous oxide: this precipitate absorbs oxygen and becomes yellow from the formation of uranic oxide, which unites with the excess of alkali. *Sulphuretted hydrogen* produces no precipitate, but *ammonic hydric sulphide* occasions a black deposit of sulphide of uranium. *Ammonic oxalate* gives a

greenish-white precipitate of uranous oxalate. Solutions of the green salts of uranium absorb oxygen rapidly, and are converted into uranic salts by nitric acid even without the aid of heat.

2.—*The uranic salts* are yellow. Their solutions give with *ammonia*, a yellow precipitate consisting of ammonic uranate, and with *potassic ferrocyanide* a brown precipitate similar in colour to that produced by the salts of copper. *Sulphuretted hydrogen* produces no precipitate, but *ammonic hydric sulphide* gives a yellowish-brown sulphide. *Carbonates of the alkali-metals* give a yellow granular precipitate, soluble in excess of the precipitant; these precipitates are double carbonates of uranium and the alkali-metal. With *infusion of nut-galls* a dark-brown precipitate is produced.

(834) **Estimation of Uranium.**—Uranium is usually estimated in the form of protoxide, to which it is reduced by heating the sesquioxide to redness in a glass tube in a current of hydrogen; the tube must be sealed up whilst full of hydrogen, and weighed in this condition, in order to prevent the protoxide from reabsorbing oxygen from the air.

Uranium is separated from the alkalies by converting it into a uranic salt by nitric acid, if not already in that condition, and then precipitating it in the form of ammonic uranate by the addition of ammonia, washing the precipitate with a solution of ammonic chloride to prevent its passing through the filter: on ignition it leaves the protosesquioxide, $UO.U_2O_3$. If barium, strontium, calcium, or magnesium be present, the addition of sulphuric acid separates the first two in the form of sulphates; if calcium or magnesium be present, the solution is filtered from the precipitate, the filtrate evaporated to dryness, and then heated with alcohol of density 0·900; the uranic sulphate is dissolved, leaving the calcic and magnesic sulphates.

Aluminium, glucinum, zinc, cobalt, and nickel may be separated from uranium by adding hydric potassic carbonate in excess to the acidulated solution: a uranic potassic carbonate remains in the liquid, whilst the earths, and other metallic oxides, are precipitated. For the success of this experiment it is necessary, if salts of ammonium be present, that they should be expelled by evaporating the solution to dryness and igniting the residue, before effecting the precipitation of the various bases with the hydric potassic carbonate.

§ IV. IRON: Fe″=56.

(835) **IRON** (Ferrum): *Density*, 7·844; *Dyad in the ferrous Salts, as* $FeCl_2$; *Tetrad in* FeS_2; *Pseudo-triad in the ferric Salts as* Fe_2Cl_6 $\left[\begin{matrix}Fe'''Cl_3\\Fe'''Cl_3\end{matrix}\right]$.—Iron is more extensively diffused than any other metal: not only is it abundant in the inorganic creation, but it is an essential constituent in the blood of vertebrate animals.

(836) **IRON ORES.**—Iron has been occasionally found in the native form accompanying the ores of platinum, and in small

grains or veins imbedded in basaltic rocks or trap, as at Giant's Causeway, at Disco Bay in Greenland, and in Auvergne, &c. When it occurs in the metallic state, however, it is usually met with in meteoric masses associated with nickel, cobalt, and small quantities of other metals, among which are copper, manganese, and chromium. Some of these masses which have fallen in an ignited state on to the earth are of very considerable size. One discovered in Siberia, by Pallas, weighed 725 kilos., or 1600 lb., and a block found in the district of Chaco-Gualambra, in South America, is estimated at between 13 and 14 tons weight. These extraordinary bodies are unimportant as sources of iron.

Aërolites, or meteoric stones, may be subdivided into three principal groups, the first of which consists of metallic masses, and these are the most common: the second variety contains no metallic iron, but consists often of crystalline minerals; and the third not uncommon form is composed of a mixture of the metallic and earthy variety in the same specimen. These different kinds of aërolites are usually inclosed in a thin crust or rind of a millimetre or two in thickness, presenting a glossy, pitch-like, or veined surface. The crystalline minerals which have been observed are of a basaltic nature, and consist of olivine, varieties of augite and leucite, anorthite and labradorite; in addition to these, chrome iron, tinstone, magnetic iron ore, and magnetic pyrites have been found, besides nickeliferous metallic iron.

The masses of meteoric iron themselves also display a crystalline structure. When a polished surface of one of these metallic masses is immersed in nitric acid, the different portions of the surface are unequally acted upon, as was first noticed by Widmannstatt: and a series of lines crossing each other in three different directions become developed; between them are broad shallow spaces, less deeply etched, and narrow bands between these retain their polish and resist the acid; these bands contain more nickel than the rest of the mass.

The origin of these meteorites is unknown; but it is an opinion generally received, that they are asteroïds or planetary dust, fragments of which from time to time come within the sphere of the earth's attraction: these, by friction in their rapid flight through the earth's atmosphere, become ignited, and if not entirely dissipated by the heat developed during their passage they ultimately reach the surface of the earth.

Amongst the constituents of these meteorites twenty-two elementary substances have been found, but no element not previously known to be of terrestrial origin has been discovered. The following are the meteoric elements, partly in the earthy, partly in the metallic portions:

Iron.	Magnesium.	Arsenicum.
Cobalt.	Calcium.	Phosphorus.
Nickel.	Potassium.	Nitrogen.
Chromium.	Sodium.	Sulphur.
Manganese.	Aluminium.	Oxygen.
Copper.	Titanium.	Chlorine.
Tin.	Silicon.	Bromine.
	Carbon.	

The metallic portions consist chiefly of native iron, which contains sulphur, phosphorus, carbon, manganese, magnesium, nickel, cobalt, tin, and copper.

The ores of iron are numerous. The most valuable are the following:

1.—*Magnetic iron ore,* or *Loadstone,* $FeO.Fe_2O_3$: *Density,* 5·09.—This is found in enormous masses, or even mountains, amongst the primary formations, and when pure contains 72·4 per cent. of iron. Much of the best Swedish iron is obtained from this material, which is also abundant in North America, in the Ural Mountains and in Piedmont, although very little of it occurs in this country. Occasionally it is found in detached octahedral crystals. Coal is absent in the formations which contain this mineral, so that charcoal is the fuel ordinarily employed in smelting it. This fuel contains a smaller amount of ash than coal; fewer impurities are therefore introduced by it during the smelting than when coal is used, and as the ore itself is generally very pure, the metal which it furnishes is of excellent quality. The heavy lustrous black *iron sand* found at Nellore, in India, and employed in the manufacture of wootz, consists chiefly of magnetic oxide of iron.

2.—*Specular iron ore,* or *Fer oligiste; Density,* 5·2.—This is an anhydrous sesquioxide of iron, Fe_2O_3: it occurs in the primary rocks. The principal part of the celebrated Elba iron, and also a large quantity of Russian and of Swedish iron, are obtained from this source. Charcoal, in this case also, is the fuel employed.

3.—*Red hæmatite,* Fe_2O_3, *Density* about 5·0, is another form of the anhydrous sesquioxide, occurring most abundantly in Cambrian, Silurian, and Devonian rocks; it is sometimes found massive, but more generally in fibrous crystalline nodules. It is usually associated with siliceous impurities, or with aluminium, calcium, or magnesium, so that 60 to 65 per cent. of iron is a fair quantity in commercial samples, although the pure mineral contains 70 per cent. This ore is largely raised in Whitehaven, and in some parts of Cornwall, but the most important deposit in Britain is in the neighbourhood of Ulverstone in Lancashire: near Cleaton Moor the bed varies from 15 to 60 feet in thickness, and the ore is very free from phosphates, so that it is in great demand for the manufacture of Bessemer pig. Vast deposits also exist near Bilboa in Spain, and in America on the shores of Lake Superior, and near St. Louis in Missouri. It is seldom melted alone, except for special purposes, but it forms a valuable addition to the clay iron-stone of the coal-measures.

4.—*Brown hæmatite,* $2Fe_2O_3.3OH_2$; *Density* about 3·9.—This is a hydrated sesquioxide of iron, which generally occurs in fibrous

or in compact masses. It is, however, also met with in the oölitic strata, in some parts of France, in the form of rounded masses, termed *pea-iron ore*, mixed with a small proportion of clay. Much of the French and Belgian iron is obtained from this source. Brown hæmatite is readily soluble in hydrochloric acid, and is less refractory in the furnace than the preceding variety. The brown hæmatite, when roasted, becomes porous from the loss of its water, and is thus rendered more manageable. Mixed with variable proportions of earth or clay, and sometimes with oxide of manganese, this oxide of iron forms the varieties of umber and ochres. It occurs principally in the secondary and tertiary deposits; the most important British deposits of this ore being those of the Forest of Dean in Northamptonshire.

5.—*Spathic iron*, or *Ferrous carbonate*, $FeCO_3$; *Density*, 3·8.—This contains from 35 to 48 per cent. of iron, and is found in crystalline masses often combined with magnesic carbonate, and with a considerable proportion of manganese, as in the Saxony ores. The most famous locality for this ore is the Erzberg near Eisenerz in Styria, but it is also found in England, as at Weardale in Durham, the Brendon Hills and Exmoor. Much of the so-called *natural steel* is made from this ore.

6.—*Clay ironstone*, although the poorest and worst of the iron ores worked, is the chief source of the enormous quantity of iron manufactured in Great Britain, from the fact that it occurs abundantly in the British coal-measures. It is an impure ferrous carbonate, containing generally from 30 to 33 per cent. of metallic iron, mingled with varying proportions of clay, oxide of manganese, lime, magnesia, and organic matter, the last named being the main source of the worst impurity of these ores, namely, the phosphoric acid. This argillaceous ironstone occurs in the coal-measures in bands broken up into nodules, or in continuous seams, from 5 to 35 centim. (2 to 14 inches) thick, alternating with beds of coal, clay, shale, or limestone. It is diffused over large areas in North and South Staffordshire, Yorkshire, Warwickshire, Derbyshire, Worcestershire, South Wales, and some other parts of Great Britain; it is also found in the United States, and in Bohemia and other countries of central Europe. It has a density ranging between 2·7 and 3·47.

7.—*The black-band* of the Scotch coal-fields, which was not largely worked until as late as 1830, is also a ferrous carbonate, but the principal foreign matter in this mineral, which often amounts to 20 or 25 per cent., is of a bituminous or combustible nature. The Airdrie bed in Scotland extends over an area of

about ten square miles, and the mineral is also found in thick seams in North Staffordshire.

8.—A siliceous ironstone containing both ferric oxide and ferrous carbonate has been found abundantly in the oölite in the neighbourhood of Northampton. It yields an inferior iron, owing to the presence of a large quantity of phosphates in the ore.

9.—Another, but comparatively an unimportant ore, of a brown colour, known as *bog-iron ore,* is a mixture of hydrated ferric oxide and phosphate in variable proportions, and appears to consist largely of fossil microscopic vegetable forms. It occurs near the surface in marshy alluvial districts in Sweden, Norway, and in Lower Canada.

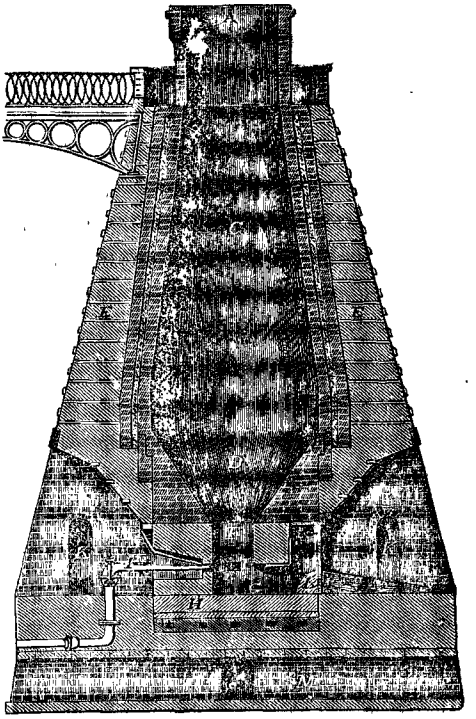
10.—*Ilmenite* is a dark grey massive iron ore found abundantly in Norway. It consists of ferric oxide with varying proportions of titanic acid.

Iron pyrites, FeS_2, although a very abundant mineral, was formerly wrought only for the sake of its sulphur, because the iron which is furnished was not pure enough for use. Now, however, by roasting the residue after burning, with common salt, the small quantity of copper and other metals, as well as the residual sulphur, are completely extracted, and a pure oxide of iron is obtained, largely used for lining puddling furnaces.

(837) **SMELTING OF CLAY IRONSTONE.**—After the ore has been broken up into masses about the size of two fists, it is generally roasted, in order to expel water and carbonic anhydride; the mass is thus left in a porous state, highly favourable to its subsequent reduction in the furnace. The roasting is sometimes performed in kilns, but usually in heaps in the open air. If this operation is to be effected in the open heap, a plat of ground is levelled and covered with a layer of coal in lumps to the depth of 25 or 30 centimetres (10 or 12 inches); this is succeeded by alternate layers of the mineral and of small coal, in the proportion of about $2\frac{1}{2}$ to 3 cwt. of coal to each ton of ore. The quantity of coal required in the case of the black-band is often very small, as the ore itself frequently contains sufficient inflammable matter to continue burning when once well lighted. The heap, when finished, is from 4·25 to 4·5 metres wide, 2·5 to 3 metres high (or about 14 or 15 feet wide and 8 or 10 high), and is of great length. The fire is kindled at the windward extremity, and allowed to spread gradually through the mass. This preliminary operation occupies some months for its completion. The roasted ore is then ready for the smelting.

The *blast furnace** employed for this purpose is represented in section in fig. 354. The internal cavity in shape resembles a long narrow funnel inverted upon the mouth of another shorter funnel; the more modern furnaces are, however, nearly cylindrical, and contracted at the top and the bottom. These furnaces are usually about 15 metres or 50 feet high, and from 4·25 to 5 metres, or from about 14 to 17 feet, in diameter in the widest part of the cavity; but they vary considerably in size and proportions, the tallest furnaces being usually employed for the reduction of the poorest and most impure ores, whilst the smallest and shortest are used for making charcoal iron from rich oxides. The lowest portion, F, or neck of the funnel, is termed the *crucible* or *hearth*, and is made of very refractory gritstone. In the front, 20 or 25 centimetres (8 or 10 inches) from the floor, H, is a longitudinal aperture above the *tymp-stone*, or *dam-stone*, L, for the overflow of the cinder or slag, and on the sides are the *tuyère holes* or openings for the *tuyères* or 'twyers,' I, I, or blast-pipes, varying from 2 to 6 in number, which are connected with powerful blowing machines for supplying air under a pressure of from 2 lb. to 3 lb. upon the inch. A steady and most

FIG. 354.



* The size and power of some of these furnaces is enormous. In the Cleveland district in 1871 there were 70 furnaces at work within 4 miles of the centre of Middlesborough, some of which are 100 feet high, 30 feet internal diameter, and 40,000 cubic feet in capacity, and making from 400 to 500 tons of pig iron per week each. The furnaces working the Ulverstone hæmatite are not so large as these, but the ore being very rich, the yield of iron is even greater: it is recorded that a furnace at Barrow-in-Furness yielded 90 tons per diem. The total number of furnaces in the kingdom in 1871 was 897, of which 673 were at work, the remainder being under repair or abandoned.

intense heat is thus uniformly maintained. At the lowest point of the furnace is the *tap-hole,* for drawing off the melted metal at suitable intervals, and which, except at such times, is closed with sand and clay: K, K, are galleries, for allowing the workmen free access to the tuyères and lower portion of the furnace, the base of which is kept dry and well drained by the arched channels, M. Above the crucible the furnace suddenly widens, forming the *boshes,* D; the lining, C, is formed of firebricks, which are continued up to the throat, A, of the furnace, the upper cone from the widest part to the throat being termed the *stack:* the whole is cased in solid masonry, E, E, and supported by iron bands.* When working regularly, such a furnace is charged through the opening, B, near the top, at intervals, first with coal, and then with a suitable mixture of roasted ore and of a limestone flux broken into small fragments, the materials being wheeled in from a gallery, or raised by means of a steam or hydraulic lift. As the fuel burns away, and the materials sink down gradually, which is facilitated by the conical form of the stack, fresh layers of fuel, and of ore and flux, are added; so that the furnace becomes filled with alternate layers of each.

The principal substances which are acted upon in such a furnace are the following:

1st, the oxygen contained in the air of the blast; 2nd, the roasted ore—consisting of oxide of iron, silica in the shape of sand or quartz, clay or aluminic silicate, and a little magnesia and oxide of manganese, the poor ores being mixed with the richer so as to average about 50 per cent. of their weight in iron; 3rd, coal or coke—composed chiefly of carbon, with a small proportion of hydrogen; and 4th, calcic carbonate or limestone, which in the heat of the furnace soon becomes quicklime.

(838) **Theory of the Blast Furnace.**—The chemical changes may be traced as follows, beginning at the bottom of the furnace:—The oxygen contained in the air of the blast, as soon as it comes into contact with the fuel in the crucible, combines with the carbon and forms carbonic anhydride, attended with the production of intense heat. The blast is thus deprived of all its free oxygen; nearly the whole of the nitrogen escapes unchanged, but the carbonic anhydride, in its passage over the ignited fuel, is

* The most recent furnaces are not nearly so conical externally as the one represented, the walls being much thinner at the base; but in order to enable these tower or cupola furnaces to resist the internal pressure or *thrust* of the charge, they are bound together with wrought-iron riveted plates, strengthened again by strong iron bands.

decomposed; each molecule of the anhydride combines with an additional atom of carbon, and becomes converted into carbonic oxide; for each volume of carbonic anhydride, 2 volumes of carbonic oxide are produced. This formation of carbonic oxide is attended with a large absorption of heat, so that the temperature of the furnace above the crucible becomes rapidly reduced, and a quantity of highly combustible gas is thus formed.* This carbonic oxide becomes mingled with carburetted hydrogen and free

* Bunsen and Playfair, in their examination of the gases produced in a hot-blast furnace at Alfreton, found that a considerable amount of potassic cyanide was formed in the hotter portions of the furnace (*British Association Reports*, 1845, p. 182); part of the nitrogen, derived probably both from the blast and from the coal, had therefore entered into combination with carbon, and had united with the potassium contained in small quantities in the ore and in the ashes of the coal.

The furnace in which these experiments were made was 12 metres, or 40 feet, deep from the top of the charge to the hearthstone, and was charged every twenty minutes with 420 lb. of calcined clay ironstone containing about 60 per cent. of oxide of iron, 390 lb. of coal, and 170 lb. of limestone: each charge yielding 140 lb. of pig-iron. The blast was under a pressure of 6·75 inches of mercury, and had a temperature of 330° (626° F.).

These chemists state that at a height of $2\frac{3}{4}$ feet from the tuyère, or 34 feet from the top of the furnace, the gases which they collected contained 1·34 per cent. of cyanogen. The following table furnishes a summary of the results which they obtained:

Analysis of Gases from a Hot-blast Furnace.

Depth from the top Height from tuyère	5 feet. 32	8 29	14 23	17 20	20 17	24 13	34 $2\frac{3}{4}$
Nitrogen	55·35	54·77	50·95	55·49	60·46	56·75	58·05
Carbonic anhydride	7·77	9·42	9·10	12·43	10·83	10·08	0·00
Carbonic oxide ...	25·97	20·24	19·32	18·77	19·48	25·19	37·43
Marsh gas	3·75	8·23	6·64	4·31	4·40	2·33	0·00
Hydrogen	6·73	6·49	12·42	7·62	4·83	5·65	3·18
Olefiant gas ...	0·43	0·85	1·57	1·38	0·00	0·00	0·00
Cyanogen	0·00	0·00	0·00	0·00	0·00	trace.	1·34
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The process of coking, which is effected in the upper part of the furnace, did not appear to be complete until the charge had reached a depth of 24 feet, but was most active at a depth of 14 feet; the principal reduction of the ore seemed to take place just below the point at which the coking was completed: the maximum heat of this furnace occurring at about 1 metre, or between 3 and 4 feet above the tuyère, or 33 feet from the top.

In a furnace fed with charcoal, Bunsen found the reduction of the ore to commence nearer the throat of the furnace, for in this case no absorption of heat occurred similar to that occasioned by the process of coking the coal, which takes place in the upper part of the hot-blast furnace. The body of a charcoal furnace consequently does not require to be so high as that of a furnace in which coal

hydrogen, which are derived from the fuel contained in the upper part of the charge, as it gradually descends towards the focus of intense heat below.* A proportion of the gases which escape from the opening at the top of the furnace, varying from 35 to 40 per cent., is combustible; the remainder consists principally of nitrogen, with a small amount of carbonic anhydride. The ore having been rendered porous by the previous roasting, is easily penetrated by these ascending gases, by contact with which the iron becomes reduced in the upper part of the furnace where the heat is scarcely a dull red, forming a spongy metallic mass. By degrees the reduced metal, mixed with the limestone and the earthy matter of the ore, sinks down to the hotter region. At a red heat the limestone is decomposed, and the carburization of the iron commences, the carbon being derived from the carbonic oxide, which at a high temperature becomes dissociated into carbonic acid and carbon, the latter uniting with the spongy metal; but between this point and the boshes, there is a zone of heat of great magnitude where the silica and phosphates become reduced and the liberated silicon and phosphorus combine with the still spongy metal, as do also the sulphur, arsenicum, and other impurities which may happen to be present. The final action consists in fusing the earthy matters to form the cinder or

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is used. Similar experiments by Ebelmen lead to conclusions substantially the same.

The following are the results of the analysis made by Rinmann and Fernquist of the gases from a Swedish charcoal blast-furnace at Hasselfors in Nerike. It was 35 feet high, the pressure of the blast 10·5 lines, and its temperature 200° (392° F.). White iron was made and the waste gases were collected.

Height from tuyère	2·0	6·0	10·0	22·4	30·1	35·0
Nitrogen	58·6	55·8	59·9	62·1	62·9	20·8
Carbonic anhydride ...	11·7	14·5	8·3	3·5	4·1	1·4
Carbonic oxide ...	24·5	23·0	28·4	31·8	31·4	35·9
Marsh gas	0·5	1·0	0·4	—	—	—
Hydrogen	4·7	5·7	3·0	2·6	1·6	1·9

* Some of this hydrogen, however, is derived from the moisture of the air, for although the proportion is but small, the actual amount passed into the furnace by this means is considerable. About 5 tons of air, containing on an average 60 lb. of water, are blown into a Cleveland furnace for every ton of iron produced, so that in a furnace turning out 50 tons of pig-iron per day, 250 tons of air containing about 3000 lb. of water pass through the furnace daily, and is there decomposed by the incandescent carbonaceous matter, yielding carbonic oxide and hydrogen.

slag,* and in the boshes the carbide of iron melts also and sinks down below the tuyères, through the lighter vitrified cinder, and is protected by it from the further action of oxygen. The bulk of the cinder is 5 or 6 times as great as that of the iron produced: it floats above the melted metal, and is allowed to flow over continually at the opening left for the purpose; whilst the iron is run off at intervals of 12 or 24 hours, by withdrawing the stopping of clay and sand from the tap-hole at the bottom.

The furnace cinder constitutes an imperfect species of glass, which is sometimes more or less distinctly crystalline, and which varies in colour with its composition, being usually opaque and grey, but often tinged blue, green, brown, or black. It consists principally of calcic, magnesic, and aluminic silicates, with generally a small proportion of manganous and ferrous silicates. In the formation of this cinder the siliceous matters of the ore react upon the earthy bases; lime, magnesia, and alumina, and readily neutralize them.

The general composition of these cinders may be seen from the subjoined analyses: I. A cinder obtained from Merthyr Tydvil, by Berthier. II. A cold-blast cinder, Tipton, Staffordshire, by D. Forbes. III. A hot-blast cinder from coke-furnace, by Percy. IV. Average of cinder from 13 blast-furnaces at Dowlais, by Riley; the last three quoted from Percy's *Metallurgy*, vol. ii. pp. 497 and 499.

Constituents.	I.	II.	III.	IV.
Silica	40·4	39·52	37·91	43·07
Alumina	11·2	15·11	13·01	14·85
Ferrous oxide	3·8	2·02	0·93	2·53
Manganous oxide		2·89	2·79	1·37
Lime	38·5	32·52	31·43	28·92
Magnesia	5·2	3·49	7·24	5·87
Potash		1·06	2·60	1·84
Calcic sulphide	traces.	2·15	3·65	1·90
Phosphoric anhydride ...				traces.
	99·1	98·76	99·56	100·35

The oxygen in the bases of these cinders is nearly equal in amount to that contained in the silica. Those quoted from Percy approach the formula, $12(CaMgMnFe)O.2Al_2O_3.9SiO_2$.

* The words cinder and slag are often used as synonymous terms by the chemist; the technologist, however, employs the word *cinder* to signify what *trickles* or flows out, *slag* what is knocked out.

The composition of No. I. may be represented by the formula, $15(CaMgFe)O.2Al_2O_3.11SiO_2$.

There are several points which require nice adjustment in this process of reduction. The cinder must not be of too fusible a description, otherwise the iron falls to the bottom before it has thoroughly combined with the carbon, and is not completely melted; a sufficiency of lime should always be present to neutralize the whole of the silica, for unless this be attended to, a ferrous silicate is formed, and iron runs off in waste. An excess of lime is sometimes advantageous, as under certain circumstances it appears to remove a portion of the sulphur from the materials employed, as calcic sulphide. At the same time the calcareous matter must not be too abundant, otherwise the working of the furnace is obstructed; the cinder which is formed being of a less fusible character is but imperfectly melted, the iron is entangled within it, and is again partially oxidized by the blast, so that the product of the furnace is greatly diminished. Experience has shown that the cinder (which is chiefly composed of the mixed calcic and aluminic silicates) is most fusible when the oxygen of the silica amounts to double that in the bases with which it is combined, and when the proportion of lime employed is such as would be furnished by adding 2 parts of limestone for every 3 of clay contained in the ore; the ratio of lime to alumina being $6CaO : Al_2O_3$. The lime is here said to act as a flux, (from *fluo*, to flow,) or material used to liquefy the clay. A cinder of this kind, however, can only advantageously be formed when the ore is smelted with charcoal, a fuel which contains but little sulphur, and which allows the reduction to be effected at a comparatively moderate temperature. When coal or coke is used as the fuel, an excess of lime is required to carry off the sulphur introduced by the pyrites of the coal, and the cinder which is produced under these circumstances is found to work most advantageously when the proportion of oxygen in the bases is nearly equal to that of the silica. The temperature of a blast-furnace fed with coal or coke is much higher than that of one in which charcoal is used. A cinder containing several bases is more fusible than when one or two only are present, the different silicates aiding the fusibility of each other. These cinders are found to be very useful as ballast for railways, since the sleepers are preserved from insects by the alkaline nature of the material: it has been recently suggested to cast the cinder in small blocks and to use them for building purposes. For a summary of an extensive experimental inquiry into the composition and properties of cinders, the

reader is referred to Percy's *Metallurgy*, vol. i. pp. 20—49, and vol. ii. p. 497.

In the process of smelting it is also necessary to proportion the supply of air rightly; if too much be thrown in, the furnace becomes unduly cooled; if too little, the supply of oxygen is insufficient to produce a vigorous combustion and the temperature consequently sinks. These, however, are points, the successful regulation of which can only be acquired by experience. The stream of air for the blast is not supplied in intermitting gusts, but is equalized as much as possible: where the cold blast is used, this object is attained by employing an air-chamber or reservoir; and where the hot blast is employed, the long pipes required for heating the air answer the same purpose.

(839) **The Hot Blast.**—The mass of air which passes through some of these furnaces is enormous, being not less than 4750 cubic metres, or about 6000 kilos. (nearly 6 tons weight) per hour. It is evident, therefore, that this immense volume of air must exercise an extraordinary cooling effect upon the contents of the furnace. This evil has been much reduced of late years by the introduction of air which has been previously heated. In this contrivance, the invention of Neilson of Glasgow, and which is known as the *hot blast*, the air, before it reaches the furnace, is made to pass through a series of pipes which are maintained at a high temperature, either by means of a separate furnace, or by a portion of the waste heat of the blast furnace itself; in the latter case the hot gases are conveyed through flues which pass from the upper part of the furnace into the chamber which contains the pipes; the necessary draught being maintained by a chimney furnished with a damper. A jet of the blast as it enters the furnace should have a temperature sufficiently high to melt a strip of lead when held in it. The temperature of such a jet as it issues from the tuyère is somewhat higher than 325° (617° F.). Mr. Siemens has improved upon this plan by passing the gases which escape from the furnace, through a *regenerator*: this is simply a chamber of brickwork filled with fire-bricks so arranged as to allow the heated gases to circulate freely around them. Two such chambers are prepared; as soon as the bricks in one of these chambers are red-hot, the current of gas from the furnace is cut off, and directed into the other chamber, in order to heat it. In the meantime a current of cold air is forced through the heated chamber, so that blast-furnaces are now worked with a hot blast, having a temperature of from 650° to 700° (1202° to 1292° F.). Each chamber is worked alternately; the one becoming heated whilst the other

is employed in heating the blast. In this way a large proportion of the heat of the waste gases may be economized.*

The saving of fuel effected by the employment of the hot blast is very great. According to Lowthian Bell only 30 cwt. of coke are required per ton of iron with the hot blast where 40 cwt. would be required for the cold blast. This saving is effected owing to the operation of several causes, one of which is, that raw coal may now be used in the furnace instead of coke: moreover, as a smaller quantity of fuel is required in the furnace to raise the injected air to the necessary temperature, so also a smaller quantity of air is needed to maintain the combustion: combustion takes place within a shorter time, so that the maximum heat of the furnace is obtained lower down in the 'crucible,' and the upper portions of the furnace do not become so intensely heated: the fusion of the metal consequently takes place nearer to the bottom, and the heat is concentrated and economized. Further:

In every metallurgical process a particular temperature must be attained in order to secure the occurrence of the reaction, or of the fusion which is desired. All fuel consumed at temperatures below that point is ineffective, and is therefore burned to waste. It must be remembered that in every case of combustion where the same chemical compounds are produced, a definite weight of fuel always emits a definite amount of heat; consequently it will raise a definite weight of air, and of materials in the furnace, through a definite number of degrees of temperature:—Say that a certain weight of fuel will raise the temperature of a given charge in the furnace from 15° to 1415° (59° to 2579° F.). Now, the same weight of fuel (if we neglect the quantity of heat

* This process, as its value becomes appreciated, will no doubt come into very extensive use in a great variety of operations in metallurgy. In many cases it effects an economy of one-half of the fuel employed, and it is possible to obtain by its means a steady and uniform temperature from one not exceeding that of a full red, up to the heat required for fusing steel. It is now employed with great success both in glass-making, and in welding the joints of wrought-iron tubes. Mr. Siemens prefers to distil the coal in furnaces through which a regulated supply of air is passed, thus furnishing a mixture of gaseous hydrocarbons with carbonic oxide and the nitrogen of the spent atmospheric air, and these combustible gases are conveyed by a flue and burned at the spot where the heat is required. The gases after having done their work are passed through the regenerator above described; and in the furnace where the combustion is effected, a temperature can thus be obtained, limited at present only by the powers of the fire-brick to resist its fusing action. The gas furnace, for such it is, has already, in many cases, superseded the old coal furnace in glass-making.

absorbed by alteration of the specific heat with rise of temperature) will also raise the same charge from 350° to 1750° (662° to 3182° F.). Suppose, now, that iron required a temperature of 1500° (2732° F.) for its fusion, no amount of fuel burned so as to produce a temperature of 1415° (2579° F.) would be of any avail in effecting the fusion of the metal, whilst a comparatively small quantity, starting from the initial temperature of 350° (662° F.) would produce the desired result.

Even in a hot-blast furnace, however, the quantity of fuel which is wasted is enormous. Bunsen and Playfair, from their elaborate experiments at Alfreton, make the almost incredible estimate that somewhat more than four-fifths of the total quantity of heat producible from the fuel consumed is lost, owing to the escape of unburned combustible matter in the form of gases, such as carbonic oxide, carburetted hydrogen, and hydrogen, which are still fit for use. Since the publication of these researches, Mr. Budd and other ironmasters have economized a portion of the heat contained in the escaping gases, in heating the blast and in generating steam.

The cold blast, which is still used for the manufacture of certain qualities of iron branded 'cold blast,' produces iron which is superior in tenacity to that obtained by the use of the hot blast; a circumstance which appears to be partly due to the fact that the proportion of silicon is greater in hot than in cold blast iron; it is also to be noticed, that in the employment of the hot blast, uncoked coal is used, a fuel which contains more sulphur, and possibly also more phosphorus, than coke, which is required in working with the cold blast.

In a hot-blast furnace of a capacity of 6000 cubic feet, 103 tons of ironstone and limestone represent 24 hours working, and this requires about 50 tons of coke. The calcined clay ironstone and limestone are mixed in the proportion of about 50 cwt. of the former to 12 cwt. of the latter (J. L. Bell). Each furnace when in full activity should therefore yield about 33 tons of metal in the 24 hours, for a common yield of the ironstone is 40 per cent. Every morning and evening the furnace requires to be tapped: on these occasions the iron is run into shallow grooves in sand, and forms the cast iron, or pig-iron of commerce. A good furnace, if well managed, may be made thus to work uninterruptedly without repair for many years.*

* It was estimated in 1855, by Mr. Blackwell, that the annual production of iron in different countries was then as follows:

(840) **Varieties of Cast Iron.**—The iron as it runs from the furnace, however, is not a pure carbide or carburet, for in the intense heat, not only is the iron reduced, but portions also of silicon, aluminium, and calcium, and occasionally other bodies derived from the flux and from the fuel. These bodies, such as sulphur and phosphorus, enter in small quantity into combination with the iron, the properties of which they modify materially. Manganese generally accompanies the ores of iron in greater or less quantity, and frequently combines with the reduced metal. Cast iron differs greatly in quality; the differences observed in it depending in part upon differences in the proportion of carbon and silicon which it contains. The composition of these carbides varies considerably within certain limits; but it does not appear that iron is capable of combining with more than about 5 per cent. of carbon. A compound of carbon having the composition of Fe_4C, or the *tetraferrocarbide*, would consist of 94·92 of iron, and 5·08 of carbon; and this is very nearly the composition of the hardest and most fusible kind of white cast iron, termed by the Germans *spiegeleisen* (or mirror iron), from the circumstance of its crystallizing in flat brilliant tables. Faraday and Stodart found the most highly carburetted iron which they could produce to consist of—iron, 94·36; carbon, 5·64. Gurlt (*Chem. Gaz.*, 1856, p. 231) has described another definite form of cast iron, Fe_8C, the *octoferrocarbide*, which when pure contains 2·63 per cent. of carbon. It has a density of 7·75, is of an iron-grey colour, and has a hardness much inferior to that of the tetraferrocarbide, being slightly malleable. It crystallizes in confused octahedral groups, and according to Gurlt is the principal constituent of grey cast iron. The existence of this compound is probable, but cannot be regarded as absolutely proved. In most varieties of cast iron the carbon exists in two distinct forms—

	Tons.		Tons.
England ...	3,000,000	Belgium	200,000
France	750,000	Russia	200,000
North America ...	750,000	Sweden	150,000
Prussia	300,000	Germany	100,000
Austria	250,000	Other states ...	300,000

In all, six millions of tons, of which Great Britain supplied one-half. Since then there has been a very great increase: in 1865 the production of iron in Great Britain was 4,819,254 tons, and in 1871 it had increased to 6,627,179 tons of pig-iron, which rose to 6,741,929 in 1872, but has since declined to 6,566,451 in 1873, and 5,991,408 in 1874.

one portion being chemically combined with the metal, the other being mechanically diffused through it in the condition of graphite, the scales of which may be seen distinctly with a magnifying lens, when the surface of a freshly fractured bar is examined. These scales remain unacted upon when the metal is dissolved in diluted acids; the combined carbon under such circumstances unites with hydrogen, and forms an oily-looking liquid of a disagreeable odour.

Spiegeleisen, as above mentioned, is a highly carburetted white iron, with a brilliant crystalline fracture. It is made principally from spathic ore, and contains an unusually large proportion of combined carbon, and also a large percentage of manganese; according to Gurlt its density is about 7·65. It is very free from phosphorus, and is largely used in the manufacture of Bessemer steel.

In addition to carbon, cast iron also contains silicon, the proportion of which is equally liable to variation; the quantities of silicon which have been found in pig-iron range between 5·6 and 0·25 per cent. It is probable that the silicon, like the carbon, is present in cast iron in two different modifications, which behave differently when the iron is dissolved in acid, but this point has not yet been definitely settled.

Karsten found that when cast iron was melted with sulphur in a covered clay crucible, there was formed, on cooling, a layer of ferrous sulphide upon the surface, then a layer of graphite, and beneath this a layer of carbide of iron in the maximum degree of carburation. These effects may be thus explained:—Carbon is incapable of decomposing ferrous sulphide, but sulphur can displace carbon from the carbide. On the addition of sulphur to the melted cast iron the carbon gradually becomes concentrated in that part of the iron not combined with sulphur, until its point of saturation with carbon is reached, and then the graphite is separated. According to the same authority, both phosphorus and silicon act in a similar manner, phosphide and silicide of iron being formed, whilst the carbon becomes concentrated in the remainder until the excess of carbon is expelled and crystallizes in the form of graphite. When the proportion of phosphorus, of silicon, or of sulphur, is but small, the compounds which they form with the iron remain disseminated through the mass of cast iron, and exert an important influence upon its texture and tenacity.

According to Le Guen (*Ann. Chim. Phys.*, 1863, [3], lxix. 282), if good grey pig-iron be fused with 2½ per cent. of powdered wolfram, the cast iron so produced is rendered much stronger and more elastic, the tenacity being increased from 3 to 4: if the quantity of wolfram be increased to 3 per cent. the metal becomes still harder, but not so tough. It is, however, doubtful whether the wolfram acts otherwise than as a flux, which facilitates the fusion of the iron and separation of some of its impurities.

The following table will serve to illustrate the general composition of some varieties of cast iron:

	Gurlt.			Bodemann.		Abel.	
	Grey coal.	Mottled hot blast.	White Gart-sherrie.	Grey hot blast.	Mottled cold blast.	Grey French charcoal.	White Silesian, very crys.
Density	7·21	7·21	7·41	7·166	7·43	7·000	7·531
Carbon, combined ...	1·021	1·793	2·457	1·44	2·78	...	4·94
Graphite	2·641	1·110	0·871	2·71	1·99	3·40	
Silicon	3·061	2·165	1·124	3·21	0·71	0·80	0·75
Sulphur	1·139	1·480	2·516	trace	trace	0·05	trace
Phosphorus ...	0·928	1·171	0·913	1·22	1·23	0·45	0·12
Iron	90·236	89·314	89·863	91·42	93·29	95·18	88·57
Manganese	0·834	1·596	2·715	trace	trace	...	5·38
Copper	...	...	...	...	...	...	0·24
Arsenicum	...	...	...	...	...	trace	
Cobalt	...	...	...	...	...	...	trace
Chromium	...	...	...	...	...	trace	
	99·860	98·629	100·459	100·00	100·00	99·88	100·00

Gurlt's specimens were all made in the same furnace, and with the same material; the grey at the highest temperature, the white at the lowest.

The fusing-point of cast iron varies with its composition; that of an average specimen was estimated by Daniell at 1530° (2786° F.).

In commerce, pig-iron is usually divided into eight varieties, numbered from 1 to 8, of which the three principal are *grey, mottled,* and *white.* In No. 1 pigs, the darkest and softest, the combined carbon ranges from 0·3 to 0·5 per cent., with 2 to 4 per cent. of graphite or uncombined carbon. In No. 8, the whitest and hardest pigs, there is from 2 to 4 per cent. of combined carbon, and about 0·5 of graphite, whilst in mottled pigs the combined and graphitoid carbon are nearly equal. Grey cast iron is soft; it may be filed, drilled, and turned in the lathe, and although somewhat less fusible than the white, is preferred for casting, since when melted its liquidity is more perfect. This variety is that which is generally produced from a furnace in good working order; but with the same materials the same furnace may produce any variety of iron from white to grey by altering the conditions of heating, the nature of the blast, or the pressure.* Variations in the state of humidity of the atmosphere also produce sensible changes in the quality of the iron. If grey

* Matthieu Williams mentions an instance of a furnace producing grey iron, which on being fitted with an apparatus for carrying off the waste gases immediately yielded white iron. On opening the mouth of the furnace, and thereby removing the pressure caused by the resistance to the free passage of the gases, the furnace at once began to produce grey iron again.

iron be cooled suddenly, it is often converted into hard white cast iron: this circumstance is taken advantage of in preparing *chilled shot,* which are cast from a fusible grey iron in a cold mould, and acquire great hardness upon the surface. The dark-grey iron used for castings, and termed *foundry iron,* requires the presence of more carbon than the lighter variety, or *forge iron,* used for conversion into wrought iron. The fracture of the *mottled* variety is in large coarse grains, among which points of graphite are distinctly visible; it is very tough, and is valued for casting ordnance. It may be obtained for this purpose by partially refining good grey iron. *White* cast iron contains about the same amount of carbon as the mottled iron, but nearly the whole of the carbon appears to be chemically combined with the metal. The white variety passes through a pasty condition as a preliminary to liquefaction: it is more fusible than either of the others, is lighter in colour, very hard and brittle, has a lamellar crystalline fracture, and a density varying between 7·2 and 7·6. It usually contains less silicon, but more sulphur and phosphorus than grey iron. White cast iron seems in some cases to owe its colour to the presence of manganese. A much higher temperature in the furnace, and consequently a greater consumption of fuel is required for the production of grey than of white iron. This may probably arise from the fact, that if white iron be melted and exposed to a temperature considerably higher than its melting-point, the tetraferrocarbide is decomposed, and if it be allowed to cool very gradually, a portion of the carbon crystallizes out as graphite, and grey cast iron is produced. In the process of casting heavy articles this carbon separates, and is thrown off in the form of brilliant scales, termed by the casters *kish.*

The peculiar value of iron for castings depends upon its property of expanding at the moment of solidification. It thus furnishes an admirable material for taking the most minute impressions, as is well exemplified in the beautiful castings obtained from Berlin.

Small articles made of cast iron, such as key-blocks, stirrup-irons, &c., may be rendered malleable by packing them in powdered hæmatite, then heating them to redness for a considerable time, and allowing them to cool very slowly: an easily fusible flux of potassic or sodic silicate containing a large amount of ferric oxide may also be used advantageously. In this case the oxygen of the oxide removes a portion of the carbon by a process of cementation the reverse of that which takes place during the manufacture of steel: the carbon is gradually removed from the outer layer of the metal, and is slowly transmitted from particle to particle through the solid bar, until it reaches the surface, where it undergoes oxidation at the expense of part of the oxygen of the hæmatite.

(841) **Conversion of Cast Iron into Wrought Iron: Refining.**—The pig-iron as delivered from the furnace is, as already noticed, far from pure: it contains variable quantities of carbon, silicon, sulphur, and phosphorus, besides traces of other metals, such as aluminium, calcium, and potassium. Before it can be converted into the wrought iron of commerce, it has to undergo a process for the removal of these extraneous matters. Many castings may be made at once with pig-iron, but it cannot be worked at the forge.

In order to effect the purification of the crude pig-iron, it is necessary to expose it to the regulated action of oxygen at a high temperature, so as gradually to burn off these oxidizable substances, and leave the iron. The pig-iron is sometimes first remelted in quantities of from 25 to 30 cwt., upon the hearth of a sort of forge, termed the *finery* or *refinery*, but this is now mostly superseded by what is known as 'pig-boiling,' that is submitting the pig at once to the operation of puddling instead of first refining it. The finery is a furnace, the fire of which is animated by a cold blast from a double row of blast-pipes. The sides and back of the hearth are formed of hollow iron castings, through which water is kept continually flowing. During this operation, which lasts about two hours, and is one of the most wasteful both of fuel and of iron, the metal loses from 10 to 12 per cent. of its weight. The use of the finery in this country is quite exceptional, and but of little advantage, except for the preparation of foundry iron from pigs containing too much silicon: the silicon is more readily oxidized than the carbon, so that it is this impurity which is first attacked in the refining process, and sometimes only traces of it remain; at the same time a small portion of the carbon contained in the iron is burned off as carbonic oxide; part of the iron also becomes converted into the protoxide, which unites with the silica furnished by the oxidation of the silicon, and with the sand which adhered to the surface of the cast metal: a fusible slag consisting of ferrous ortho-silicate, $2FeO.SiO_2$ or Fe''_2SiO_4 $[Si(O_2Fe)''_2]$, is thus produced. The oxide of iron in this slag again reacts upon the melted metal, and by imparting a portion of its oxygen to the silicon and carbon disseminated through the mass, burns off an additional quantity of these substances; portions of sulphur and phosphorus are also separated by oxidation in this process, and accumulate in the slag. The melted iron is then run off into a long shallow trough, usually of cast iron, and formed into a flat cake 2 or 3 inches (from about 5 to 8 centimetres) thick, and as soon as it

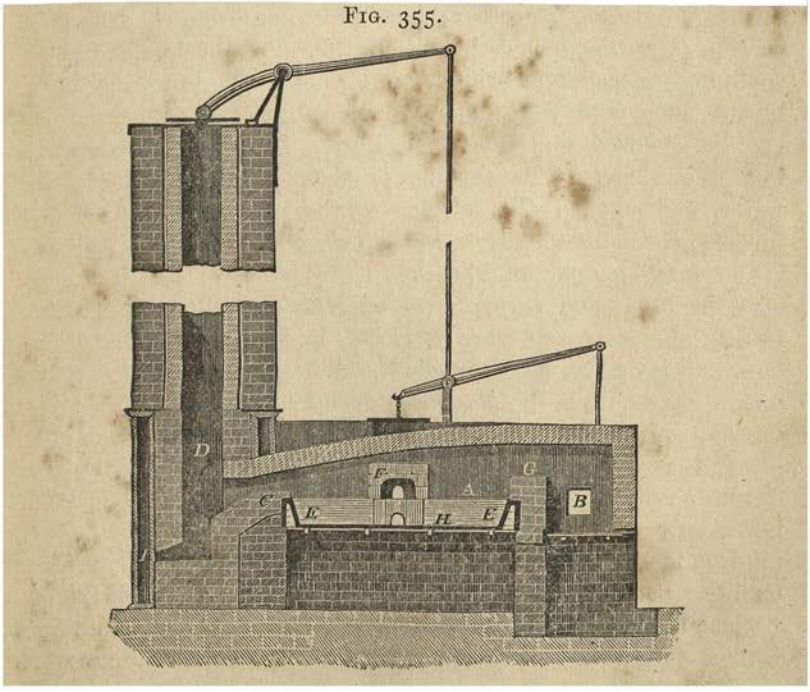
begins to solidify it is suddenly cooled by pouring water upon it; a hard white, brittle mass is thus obtained, which is broken up into fragments. In this operation, coke is the fuel generally made use of, but where iron of superior quality is required, as in making tin-plate, charcoal is employed. Ordinary coke contains sulphur and earthy impurities which injure the quality of the iron.

The effect of the operation is well exhibited by the following analysis quoted by Regnault, giving the composition of a portion of cast iron before refining, and a portion of the same metal after it had passed through the refinery furnace.

	Before refining.	After refining.
Carbon	3·0	1·7
Silicon	4·5	0·5
Phosphorus	0·2	
Iron	92·3	97·8
	100·0	100·0

(842) **PUDDLING.**—The action of the finery if sufficiently long continued will remove the silicon and carbon, and ultimately

FIG. 355.



yield malleable iron, which may be hammered out if the pig was originally free from sulphur and phosphorus. Pig-iron, however, usually contains injurious quantities of these elements, which must be removed to yield a serviceable malleable iron, and this cannot be done in a finery by simply burning them out. These impurities are removed, however, by 'puddling,' the invention of Cort in 1784. The iron, usually mottled, pig or a mixture of grey and white iron, is introduced in charges of 4¼ cwt., or about 250 kilos., into the *puddling furnace*. This consists of a reverberatory furnace, connected with a chimney 40 or 50 feet (12 or 15 metres) in height, capable of producing a powerful draught, which is under complete command by means of a damper. Fig. 355 represents a section of the puddling furnace; A, is the bed, or hearth, upon which the iron for puddling is placed; B, is the fire-place with the aperture for stoking, which is closed with coal, and not by a door, as is usual in most furnaces; G, is the bridge which separates the fuel from the metal; the hearth, A, which was formerly of sand, is now lined with cast-iron plates, E, E, which are prevented from melting by the free circulation of air beneath them, as first proposed by Samuel Rogers in 1818; C, is the flue leading to the chimney, D, at the top of which the damper is shown; H, is the plate upon which the iron rests during the puddling process; it is protected from the heat by a coating of *fettling*, consisting of pure powdered hæmatite, roasted spathose ore, magnetic oxide, or 'bull dog;' the last being made by roasting refuse tap cinder in a kiln, by which means the silicate is oxidized and converted into a mixture of ferric oxide and free silica. The fettling is ground up, moistened with water, and applied like mortar to the sides and bed of the furnace, and subsequently strewed over with loose iron scale; F, is the working door of the furnace, which is of cast iron lined with fire-brick, and through the aperture in which the puddler works; the lower aperture is closed by sand during the operation, and is opened at intervals to allow the *tap cinder* to be drawn off, and I is the *floss-hole*, or aperture through which the overflow of cinder is removed.

It is now usual to charge the furnace with pig-iron that has not been refined. Iron which has undergone the refining process never becomes so completely liquid in puddling as when crude pig-iron is employed, but the metal produced is generally of finer quality. Supposing the crude pig-iron to be used, the pigs slowly become melted, so that in from 30 to 40 minutes the metal forms a thick pasty mass, which gradually becomes fluid, and at length

perfectly liquid: this is stirred with a *rabble* or bar of iron, flattened out and bent over at the end introduced into the furnace. Presently the surface of the metal becomes violently agitated, owing to the escape of the carbonic oxide in jets, which take fire and burn with a blue flame, whilst the melted mass swells up to several times its original bulk: this process is technically known as *boiling*. The melted iron is now briskly and energetically stirred by the puddler to promote oxidation.

When refined iron is used in puddling instead of crude iron, it is often mixed with a certain proportion of scales of oxide from the forge, and is then gradually brought into complete fusion, carefully avoiding the contact of fuel. The mass is well stirred, so as to incorporate the oxide of iron with the melted metal; oxygen is transferred from the oxide thus introduced to the carbon of the melted iron, and carbonic oxide is formed abundantly; but the appearance of boiling is less marked than when crude pig-iron is used. In either case, as the carbon diminishes in quantity, the metal by degrees becomes less fluid from the gradual formation of solid particles of infusible iron, and as these become more distinctly separated, the liquid ceases to be homogeneous, and is at length converted into a granular, sandy mass. The heat is now raised until it becomes very intense, and air is carefully excluded by closing the damper and doors so that the spongy iron which absorbs oxygen with extreme avidity may be surrounded by a carbonaceous reducing atmosphere. The metal again begins to soften and agglomerate. The puddler gradually collects it into balls or *blooms* upon the end of the rabble; he then removes it from the furnace in masses weighing about three-quarters of a hundredweight, or 38 kilos., and subjects it, whilst still intensely hot, to the action either of the steam hammer or of a powerful press, called the *shingling press*. The melted slag is thus forcibly squeezed out, the particles of metal are brought nearer together, and the density is increased. The process of puddling ordinarily occupies about two hours; and provided the operation has been skilfully conducted more puddle bar can be obtained than the weight of the pig-iron put in, the excess being derived from the reduction of the oxide of iron with which the furnace is lined: the oxide of iron, moreover, materially aids in the oxidation of the carbon and silicon in the pig-iron. This increased yield, however, is not obtained in practice, a puddler producing only 4 cwt. of iron from $4\frac{1}{4}$ cwt. of pig; for although he is paid by the cwt. for the iron he turns out, the increased

yield would not compensate him for the extra time consumed in obtaining it.

The reactions which take place in the puddling furnace are not so simple as might appear at first sight, for not only is the carbon and silicon removed, but also most of the phosphorus and sulphur. It seems probable that the iron, although itself fusing at a very high temperature, is readily soluble in the more fusible carbide and silicide of iron, so that mottled pig-iron is actually such a solution of iron in carbide and silicide of iron. When this is heated in the puddling furnace, the first action is to oxidize the carbon and silicon, causing the metallic iron to be precipitated in minute particles as its solvents gradually diminish, although these particles are still wetted with the fusible sulphide and phosphide of iron. The sulphur and phosphorus, in combination with the iron, resist oxidation, but it is necessary to remove them: this is done by the puddler who, by violently stirring about the mass when it is becoming granular and sandy, washes the metallic particles with the fluid siliceous cinder and thus removes the adhering film of sulphide and phosphide of iron. This bath of cinder also serves the purpose of protecting the spongy iron in a great measure from the oxidizing action of the air.*

The iron after being shingled is fashioned into a bar by passing it between grooved rollers, and the bar thus obtained is

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* Calvert and Johnson (*Phil. Mag.*, Sept 1857) made a series of analyses of the iron in different stages of the process of *boiling*. They employed in their experiments good cold-blast Staffordshire grey iron, No. 3, such as is used for making iron wire.

	Time after charging.	Carbon.	Silicon.	Phosphorus.	Sulphur.
Pig iron		2·275	2·720	0·645	0·301
1st sample	40′	2·726	0·915		
2nd „	60′	2·905	0·197		
3rd „	65′	2·444	0·194		
4th „	80′	2·305	0·182		
5th „	95′	1·647	0·183		
6th „	100′	1·206	0·163		
7th „	105′	0·963	0·163		
8th „	110′	0·772	0·168		
9 Puddled bar		0·296	0·120	0·139	0·134
10 Wire iron		0·111	0·088	0·117	0·094

A charge of 2 cwt. of iron was introduced into the bed of the furnace without any addition of oxide of iron: in 40 minutes it became fused, and on cooling the sample suddenly, it yielded a brittle mass like white iron. It will be seen

cut into lengths, then piled up in a reverberatory furnace and re-heated; it is again rolled, doubled upon itself, and re-heated and rolled. Upon the best qualities of iron this process is repeated several times, in order to render its fibres parallel to each other, by which the toughness of the metal is much increased. The iron is now nearly pure; it contains from $\frac{1}{400}$ to $\frac{1}{200}$ of its weight of carbon, and about $\frac{1}{500}$ of silicon. The presence even of this small proportion of carbon adds materially to the toughness and hardness of the metal. When malleable iron is rolled, piled, and re-rolled several times as in the manufacture of thick plates, such as armour plates, there is great difficulty in avoiding the production of *burnt iron*. This burnt iron, instead of being tough and having the silky fibrous fracture of good wrought iron, is quite rotten, and on examining the fracture, a black dust may be observed between the fibres; this black dust consists of particles of oxide of iron, apparently magnetic oxide, diffused through the mass. When iron is piled and re-rolled it is improved in quality up to the 6th or 7th rolling, if great care be employed to prevent oxidation in the heating furnaces, but after that, the quality steadily deteriorates from the formation of burnt iron, apparently due to oxidation during the transit of the plates from the furnace to the rolls.

The cinder produced during the operations of puddling and refining consists chiefly of ferrous ortho-silicate, $2FeO.SiO_2$, and

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that whilst the carbon increases during the first stage of the process, the silicon undergoes a very rapid diminution. The 3rd sample was taken just before the beginning of the *boil*, when the iron was in its most fluid condition. No. 4 was taken during the full boil, and consisted of small detached brittle granules surrounded by slag. No. 5, the boil was completed. It was still in granules, but they were slightly malleable. No. 6, the iron was collecting into masses. No. 7 was taken during balling, and in No. 8 the balls were just ready for the shingling press. The 'puddled bar' was taken from the iron after it had been hammered; and the 'wire iron' was the same after it had been broken up into billets, re-heated, and rolled as a preliminary to drawing.

The cinder which was separated during the operation was found to have the following composition:

Silica	16·53
Ferrous oxide	66·23
Ferrous sulphide	6·80
Phosphoric anhydride (P_2O_5)	3·80
Manganous oxide	4·90
Alumina	1·04
Lime	0·70
	100·00

contains upwards of 60 per cent. of the metal. This *finery cinder* is reduced in the blast-furnace in the same manner as the original ore, but it is always found to produce a defective iron, technically known as *cold short*. Such iron may be forged well at a red heat, but when cold it is brittle and rotten. This defect is attributed to the presence of phosphorus, which is separated from the crude metal in the form of phosphate of iron during the puddling. When the cinder is reduced in the blast-furnace, the phosphide of iron accumulated in the cinder passes into the pig and forms the faulty metal in question.

(843) **Puddling by Machinery.**—Numerous attempts have been made to replace by machinery the manual labour employed in puddling, but with comparatively little success until recently. The results obtained, however, by the puddling machine invented by Mr. Danks in America are comparatively favourable, although the wear and tear is so seriously great, that many firms who had adopted the machine have since abandoned it. The apparatus consists of a revolving cylindrical chamber down the sides of which the molten iron rolls, whilst the fire is urged by a blast fan; this cylinder has a lining consisting of two layers, initial and *fettle*. The initial layer consists of pulverized ore free from silica and lime: over this is applied the fettle, consisting of ore melted by heat and allowed to flow round the interior while the chamber rotates; lumps of cold iron ore, preferably ilmenite (a titaniferous iron ore), big enough to project from 3 to 6 inches, being thrown in just before the fettle sets so as to increase its surface. The pig-iron to be puddled is then melted in a cupola furnace, and the charge, usually about 10 cwt., run into the rotating chambers, whilst a jet of water is directed against the lining on the descending side, in order to solidify a portion of the cinder, and cause it to be carried under the iron. The iron soon begins to boil violently, and the carbon quickly disappears, being oxidized by the oxygen of the iron ore used as fettle. The ball of malleable iron is then withdrawn from the chamber, and squeezed by powerful machinery specially adapted for dealing with such a large mass of metal.

Crampton's Dust Furnace.—An invention likely to prove of very great value in connexion with mechanical puddling is Crampton's dust fuel furnace, which consists of a rotating cylinder 6 feet 8 inches in outside diameter and of the same length, supported on rollers: one of the most important features in the construction being the water casing which surrounds it, serving not only to keep the initial lining solid, but also to cool the

bearings, and consequently greatly diminish the wear and tear. The fuel consists of coal ground to fine powder, which is mingled with air in an agitating chamber by means of a rotary stirrer, the mixed stream of air and coal dust being burnt in the furnace like gas. A reducing or an oxidizing flame may be produced as required by regulating the proportion of air to that of the coal dust. This rotating furnace is lined with a fettle of molten iron ore at five separate heats, so that the interior section of the drum, when lined is pentagonal so as to favour agitation. The charge consists of 8 to 10 cwt. of pig, and the conversion into puddled iron takes place in a manner very similar to that in Danks's machine: the ball, however, is hammered, which appears to be far more effectual in removing the slag than squeezing: it is, however, important to remember that it is far more difficult to separate slag or cinder from the large puddle ball turned out by these machines than from the ordinary puddle ball which is only one-sixth or one-eighth the size; on the other hand, it is contended that this large ball yields a more homogeneous iron.

Henderson's Process.—Besides the various mechanical contrivances for facilitating puddling, several chemical processes have been proposed for converting pig into malleable iron without the aid of mechanical means; the only one of any importance, however, is that of Mr. James Henderson. He places on the bottom of the furnace a layer of calcic fluoride mixed with some oxide of iron, as hæmatite, ilmenite, &c., and on this the pigs. As soon as these are melted, a violent agitation is produced by the gases evolved, the effervescence gradually increasing until the iron is completely granulated. This agitation, no doubt, acts as a substitute for that produced by the rabble in the ordinary mode of working.

(844) **Production of Wrought Iron direct from the Ore.**—The pure ores, which consist of magnetic oxide, or of ferric oxide, are frequently converted at once into wrought iron, without the production of cast iron. This process is practised in the Pyrenees, with a cold blast, by what is termed the Catalan forge, and still more largely by the *bloomery forges* of North America. In the American bloomery forges of Vermont, Quebec, &c., the hot blast is employed:—The ore having been first reduced by stampers to a coarse powder, is placed on the top of the charcoal in the forge which has been kindled for its reception; a high heap of charcoal is kept on the fire, and a gradual supply of ore is maintained; as the metal is reduced, it sinks to the bottom in a pasty state: when sufficient has been added to form a bloom, or ball, the metal is collected on an iron bar, heated before the blast-pipe, and then

hammered, rolled, and welded, as if it had come from the puddling furnace (Overman's *Metallurgy*, p. 544). This method yields a very pure iron when charcoal is employed, but the consumption of fuel per ton of metal is much greater than in the blast-furnace, being about 3 tons of charcoal in the Pyrenean and about $1\frac{3}{4}$ tons in the American forges for each ton of finished iron; a large portion of the ore is also wasted in the form of cinder, which is very rich in oxide of iron. The iron produced by this process frequently contains sufficient carbon to give to it some of the properties of steel; for instance, it becomes much harder when heated and suddenly cooled. Iron of this description is valuable in the manufacture of plough-shares, and heavy articles requiring both toughness and hardness.

Siemens' Process.—Dr. C. W. Siemens has introduced an entirely new process for the production of malleable iron direct from the ore, the apparatus employed consisting of a horizontal rotary furnace heated by means of a regenerative gas furnace, and lined with bricks made from *bauxite* mixed with six per cent. of plumbago and sufficient sodic silicate (waterglass) to form a coherent mass; the plumbago reduces the ferric oxide in the bauxite to metallic iron, and renders the bricks not only capable of withstanding in a remarkable degree the action of the fluid cinder, but also practically infusible. About 30 cwt. of the ore, broken into fragments the size of beans, is introduced together with the fluxing material into the furnace, which revolves slowly, and is there heated to a very high temperature, but not sufficient to melt the ferric oxide; about 25 to 30 per cent. of small coal of uniform size (not larger than nuts) is now thrown in, and the velocity of the rotation increased. A rapid reaction takes place: the peroxide is reduced to magnetic oxide, which begins to fuse, and at the same time spongy metallic iron is precipitated by each individual piece of carbon; the carbonic oxide evolved during this reaction is sufficient to continue the combustion, so that the supply of gas from the gas-producers may for a time be partially or entirely cut off. When the reduction is complete, the cinder is tapped off, and a rapid rotation continued, so that the particles of precipitated iron may ball together. Three of these balls are produced in each furnace by the interior lining having projecting ribs or ridges for that purpose. The masses of wrought iron (which on an average contain 70 per cent. of metallic iron and 30 of cinder) may be taken out and shingled in the usual way. This removes the bulk of the cinder, but sufficient remains to make the iron 'red short' when worked. By re-piling and re-heat-

ing several times this defect may be removed, but a far more ready method is to beat out the balls as they come from the rotator into flat slabs about 1 inch in thickness, which are then cut up and formed into blooms of about 2 cwt. each on the refinery hearth: these are consolidated under the shingling hammer and rolled into bars in the usual way. By these means, iron of very high quality may be produced directly from poor ores, but only about 75 per cent. of the iron in the ore is actually obtained in the metallic state, the rest remaining in the cinder along with the phosphorus, sulphur, and other impurities. If the ore employed is comparatively pure, however, of course the cinder and slag can be returned to the furnace in succeeding charges and much of the iron it contains recovered.

With rich ores such as hæmatites, it is more advantageous to use a stationary furnace, the mixture of pulverized ore, flux, and reducing material being charged into the heated chamber (previously coated with coke dust or anthracite to protect the siliceous lining), where it is subjected to a full welding heat in a non-oxidizing flame. In the course of two hours a thick skin of malleable iron is formed over the surface of the mass, which is removed by means of hooks and shingled and rolled. In the course of another hour and a half more metallic iron is formed, which is withdrawn and treated in the same manner, continuing the operation until the furnace charge is nearly exhausted. If, instead of removing the metallic iron as it is formed, hæmatite pig in the proportion of about 40 per cent. of the original charge be introduced into the furnace after the action has been going on for four or five hours, the malleable iron is dissolved by the pig as fast as it is formed, and after three or four hours the whole of the materials are rendered fluid. A metallic bath is thus obtained covered with a glassy slag containing about 15 per cent. of iron. After the carbon has been brought down to about 1 per cent., the proper amount of ferromanganese or spiegeleisen is added, and the metal tapped in the usual way. In this way cast steel is obtained direct from the ore, equal in quality to that produced by the open hearth process.

(845) **MANUFACTURE OF STEEL.**—Iron, when combined with a smaller proportion of carbon than is contained in cast iron, furnishes the compound well known as *steel*, of which there are several varieties; the value of steel for edge tools and similar articles being proportional to its freedom from all ingredients except iron and carbon. The quantity of carbon in good steel varies between 0·7 and 1·7 per cent.; but steel which possesses

the greatest tenacity has been found to contain from 1·3 to 1·5 per cent. of carbon, and about 0·1 of silicon. *Natural steel* is produced directly from the best cast iron free from sulphur and phosphorus by heating it by means of charcoal on the refining hearth, as in the operation which precedes the process of puddling; the oxygen burns off a portion of the carbon from the cast iron, and steel is left. In some of the Welsh ironworks steel is now made upon the bed of the puddling furnace itself, by carefully arresting the operation at a stage short of the complete oxidation of the carbon. The preparation of natural or puddled steel is, therefore, an intermediate stage in the conversion of cast into wrought iron. Iron which contains manganese is best fitted for the preparation of this kind of steel. The mass thus obtained is rendered homogeneous by forging. It yields a steel of inferior quality, which is employed for making agricultural implements and springs for machinery. *Krupp's cast steel*, made at Essen, near Cologne, is a puddled steel, containing about 1·2 per cent. of carbon. Castings of 16 tons in weight have been obtained for ordnance by pouring steel melted with a little bar iron in crucibles, each holding 30 lb., into the mould, 1200 such crucibles being required for one such casting, which is allowed to cool very slowly in the mould: this is sometimes not opened for 10 or 12 weeks.

For more delicate purposes, *blistered steel* is made use of: this is obtained by means of *cementation*, which is an operation just the reverse of that by which natural steel is formed. This process is carried on in a furnace into which are built two rectangular boxes of brickwork or stoneware, from 10 to 15 feet (3·05 to 4·60^{metres}) long, 30 to 36 inches (762 to 914$^{\text{mm.}}$) deep, and about the same width, for the reception of the bars of iron which are to be converted into steel: the fire-grate is between these boxes, around which the flame circulates freely. This conversion is effected by heating the iron in contact with powdered charcoal, or with soot, forming what is technically termed *cement powder*. In preparing a charge, the bottom of each box is covered with a layer of the cement powder to a depth of about an inch (25$^{\text{mm.}}$), and upon this a layer of bars of the best malleable iron is placed. The bars are generally about 3 inches (75$^{\text{mm.}}$) broad, and $\frac{3}{4}$ inch (18$^{\text{mm.}}$) thick, and as long as the box. The interstices between the bars are also filled with charcoal powder, which is tightly packed around the iron; above this is a layer of the powder, then another layer of bars, and so on in succession until the box is nearly full, when it contains from 6 to 9 tons of iron. The

remaining space is now covered with old cement powder (charcoal which has been already used), and finally with a layer of damp sand of from 3 to 6 inches (8 to 15$^{cm.}$) in depth, and the fire is gradually raised to a full red heat, or to about the temperature required for melting copper, 1090° (1994° F.); at this point it is steadily maintained. Some of the bars of iron are so placed that they can be removed from time to time during the operation for the purpose of ascertaining the process of the carburation by inspection; the fibrous structure of the bar gradually changing to a minute granular or crystalline structure, which is revealed by the fracture. The process is usually complete in six or eight days; but the time required necessarily varies with the thickness of the iron bars operated on: the fire is then gradually reduced, and the furnace is suffered to cool slowly, an operation which lasts ten days or a fortnight. The steel thus obtained retains the form of the iron, but it is covered with blebs or blisters, by which the surface is rendered irregular and uneven. The mass is found to have been penetrated by carbon which has been transferred from particle to particle of the metal, the properties of which it has completely changed. In some cases these blisters probably arise from the combination of parts of the carbon with oxygen derived from particles of oxide of iron, which are apt to be mechanically retained even in the most carefully prepared bars. Carbonic oxide would thus be produced, and imprisoned in the tenacious metal, which in its softened state would be raised by it into bubbles or blebs. Great care, however, is generally taken to exclude slag and oxide of iron from bars which it is intended to convert into steel; so that in the majority of instances it is not unlikely that the blisters are occasioned by the combination of carbon with the sulphur which is still retained by the iron, and which, by forming the volatile carbonic bisulphide, would produce the effect (T. H. Henry). All bar iron contains traces of sulphur; but in steel, sulphur is seldom present, and there appears to be no other mode of accounting for its general absence than its removal during the process of carburation in the form of carbonic bisulphide.

By the process of cementation, the iron has been combined with about 1·5 per cent. of carbon: it is now much more fusible than before.* It has likewise entirely lost its fibrous texture,

* According to Fremy, steel contains also, as a necessary ingredient, a minute quantity of nitrogen, which it has been suggested may be in the form of cyanogen. Caron, however, maintains that this trace of nitrogen is not essential. Rammelsberg was unable to detect more nitrogen than 20 parts in a million of cast iron. Marchand did not obtain more than 150 parts of nitrogen from a

and when broken across exhibits a close, fine-grained fracture. Steel may also be made without direct contact with carbon, by simply heating the bars in carburetted hydrogen; but this process has not come into general use. Graham has shown that iron has the power when heated to redness of absorbing or *occluding* 6 or 8 times its volume of carbonic oxide, which it retains on cooling. No doubt this power of absorbing the gas is intimately connected with the process of cementation (70 *a*).

Blistered steel is never homogeneous, the surface being always more highly carburetted than the inner portions of the bars. This variety of steel is employed for files, tools, and hardware of all descriptions. When blistered steel is fused, it forms *cast steel*, which, from being more uniform in texture, is of superior quality, as the carbon is more equally distributed throughout the mass: it is employed for cutlery of the best description. A cheaper kind called *tilted steel* is also obtained from blistered steel; this is first broken up into lengths of about 18 inches (or $45^{cm.}$), then bound into fagots and raised to a welding heat in a wind furnace, where it is covered with sand, which combines with the superficial coating of oxide of iron and forms a fusible slag: the red-hot fagot is then rolled and forged into smaller bars by means of the tilt-hammer, which weighs about 2 cwt., and strikes 200 or 300 blows per minute. All steel is improved by this process of hammering. These tilted bars, when broken up and welded together, form *shear steel.*

For many purposes the addition of a small quantity of manganese is an improvement to the quality of the steel. If about 1 per cent. of carbide of manganese, or of a mixture of charcoal and black oxide of manganese, be introduced into the melting-pot, a steel is obtained of fine close grain, which admits of being welded to wrought iron; a property not possessed by ordinary steel. The experiments of Faraday and Stodart led them to the conclusion that the addition of small quantities of chromium, or of rhodium, to good steel, furnished a steel of a superior kind.

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million parts of the metal, and often a much smaller quantity. He considered the nitrogen to be due to the accidental presence of foreign impurities, and this is certainly the most probable opinion; no instance is known in which so minute a quantity of matter is an essential constituent of any compound. Boussingault found pure iron reduced from the oxide in hydrogen gave no trace of nitrogen, by a method of analysis which indicated in soft iron 50 millionths, and in piano wire from 70 to 86 millionths, and in cast steel 57 millionths: this steel also contained traces of sulphur. The difficulty of excluding such minute traces of nitrogen in the course of the analysis is extreme, even in the hands of one who, as in this case, is confessedly a master (884).

They found that steel may be alloyed with about a five-hundredth of its weight of silver; and with platinum, as well as with rhodium, and with osmium and iridium in all proportions. The combination of 8 or 9 per cent. of tungsten with ordinary steel has been said to yield a material remarkable for hardness and elasticity, but experience does not seem to justify the expectations of its utility (Percy's *Metallurgy*, vol. ii. p. 193). A similar remark is also applicable to titanium steel (*Ib.*, p. 168). When steel is to be used for the manufacture of dies for coining, the presence of a small proportion of phosphorus is beneficial (Brande).

When dilute nitric acid falls upon steel, a dark grey spot is produced, owing to the solution of the metal in the acid whilst its carbon remains unacted upon: the acid produces a green spot upon iron. Nitric acid acts unequally upon different parts of the surface in certain of the finer varieties of steel, and thus produces a veined appearance, such as was formerly given to the celebrated Damascus blades. The Damascus steel is more highly carburetted than ordinary steel, and if allowed to cool slowly, it separates into layers of two different degrees of carburation (Bréant): hence certain parts, when acted on by diluted acid, leave more carbon than others: the form and direction of these veins vary with the mode of forging adopted.

Wootz is a finely damasked, hard cast steel, of excellent quality, which is obtained from India. Faraday found aluminium in a sample of this steel which he analysed, and was disposed to refer its peculiar qualities to the presence of this metal. It appears, however, from the experiments of Henry (*Phil. Mag.*, July, 1852), that aluminium is not always present in wootz. He gives the following as the composition of a bar of genuine Indian wootz, of density 7·727:

Carbon	combined	1·340
	uncombined	0·312
Silicon		0·042
Sulphur		0·170
Arsenicum		0·036
Iron		98·100
		100·000

Other analysts have also failed in finding aluminium in wootz.

(846) **Bessemer Steel.**—Mr. Bessemer has invented a process whereby the silicon and carbon are first burnt out of molten pig-iron, and then a quantity of *spiegeleisen* is added, containing manganese and sufficient carbon to convert the whole mass into steel; this is at once cast into ingots. By varying the propor-

tion of spiegeleisen added, all gradations of metal may be obtained, from perfect steel to wrought iron having only the slightest possible resemblance to steel.

The apparatus employed consists of an egg-shaped vessel of iron called a *converter*, lined with fire-clay or a coarse siliceous rock termed *ganister*, which is crushed, moistened with water, and applied to the interior, where it dries slowly: the flat circular bottom, which is made removable, is fitted with cylinders of fire-clay, each of these being perforated with several holes from $\frac{1}{2}$ to $\frac{3}{4}$ of an inch in diameter. The converter is mounted on trunnions for the convenience of pouring out the molten metal, and is covered by an arched head, having an opening at one side. The pig-iron is first melted in a cupola, or reverberatory furnace, and then run into the converter, where it is exposed to the action of a blast of air driven in through the 60 to 100 holes in the fire-clay bottom at a pressure of from 12 lb. to 25 lb. per square inch. An intense combustion takes place accompanied by great elevation of temperature, due chiefly to the oxidation of the carbon and silicon; the former being converted into carbonic oxide escapes at all points of the mass, throwing the whole into violent agitation as if it were boiling. The mass of flame which issues from the mouth of the converter, accompanied by dazzling showers of sparks at irregular intervals, steadily increases in size and brilliancy, attaining its maximum after about 10 minutes. At the expiration of 20 to 25 minutes the flame contracts, and at the same time changes in appearance; this marks the exact moment at which the iron is properly decarbonized, and may be determined with the greatest accuracy by a spectroscopic examination of the flame.* The converter is now turned on its side, and the proper quantity of melted spiegeleisen is poured in, containing the exact amount of carbon necessary to produce the desired quantity of steel. A violent ebullition takes place, as it

* According to Brunner and Lichtenfels, when the pig-iron contains manganese, spectroscopic examination of the flame shows three distinct periods of action. In the first, the continuous spectrum shows sodium lines in the yellow, lithium in the red, and two potassium lines in the violet, besides manganese lines between the yellow and green. In the second period, the lithium and potassium lines disappear, whilst carbon lines make their appearance, together with fresh manganese lines in the green and between the green and blue, but as the action proceeds, the manganese lines successively disappear, leaving the sodium and carbon lines. In the third period, the carbon lines in the green become weaker and suddenly disappear. In the decarbonization modification of the Bessemer process practised in Germany and Austria, the disappearance of the manganese lines indicates the period of formation of steel.

mixes with the melted metal, and a carbonic oxide flame pours out of the mouth of the converter, produced by the combustion of a small portion of the carbon in the spiegeleisen, with the particles of oxide of iron entangled in the iron in the converter; the metal is then poured into a ladle worked by a crane, and thence transferred to the ingot moulds, which are made of cast iron communicating with one another below, and are usually from 3·5 to 4·25 feet in height. The converters usually employed vary in capacity from 5 to 12 tons of metal, the air being forced in through tuyères in the bottom 0·5 to 0·75 in. in diameter, and which require frequent renewal owing to the destructive effect of the intense heat. About 500 cubic feet of compressed air is driven in for every 100 lb. of pig-iron. As sulphur and phosphorus cannot be removed from pig-iron by oxidation it is necessary to employ iron free from these impurities; a superior class of iron of this kind is now made from red hæmatite, and is known as 'Bessemer pig.'

The action of the blast on the iron in the converter first oxidizes the silicon and manganese, producing a fusible cinder of silica and manganese, whilst at the same time any graphitoid carbon present combines with the iron. When the silicon is nearly oxidized, the carbon begins to be attacked, and the action goes on increasing until it reaches its maximum when the flame is brightest. As the silicon, manganese, and carbon in a charge of 6 tons of 'Bessemer pig' usually amounts to about 8 cwt., it is easy to understand how the burning of this amount of fuel in the short space of 20 minutes produces the intense heat necessary to keep the nearly pure iron in a state of fusion. When the carbon present becomes reduced to about 0·2 per cent., the iron begins to be oxidized; it is then that the character of the flame changes, and the spiegeleisen is added. The spiegeleisen appears to do nothing more than merely supply the necessary amount of carbon to form steel; it improves the quality of the steel, however, and it has been suggested that the manganese present in it serves to remove the residual silicon. It is customary for the Sheffield makers, when melting the blistered steel, to add oxide of manganese, which causes the separation of a siliceous cinder, although the best steel when finished will be found to be free from manganese.

Dr. C. W. Siemens has recently introduced a method of making steel somewhat similar in principle to that of Bessemer, first worked with practical success by Martin, of Sireuil, near Paris. By means of the intense heat at command by the use of his regenerating furnace, he dissolves old scrap iron and malleable iron rails in a bath of melted pig-iron free from phosphorus; the proportion of

gas and air being so adjusted that the operation takes place in a reducing flame. This process affords an admirable way of utilizing scrap iron, Bessemer scrap, and other cheap material (see also p. 629). The steel thus produced is of superior quality, almost the whole of the phosphorus having been removed in the process of puddling.

(847) **Properties of Steel.**—The physical properties of steel differ materially from those of iron. As already mentioned, steel is granular in texture, brittle, and more easily melted than iron. Its most characteristic property, however, consists in its power of assuming a hardness scarcely inferior to that of the diamond, when heated to redness and then suddenly cooled by plunging it into water, mercury, or oil. After this treatment, which cast steel bears with less distortion than shear steel, owing to its being more homogeneous, it is rendered extremely brittle, and almost perfectly elastic. It can then no longer be attacked by the file. This extreme hardness and brittleness may be removed by the process of *tempering* or *letting down*, which is a peculiar mode of annealing; it consists in heating the steel moderately, and then allowing it to cool. This capacity of being hardened and tempered is the most important and characteristic property of steel, and can be modified through a regular range of gradations from that of the hardest turning tools and drills to the elasticity of watch-springs and needles; whilst in its softest state it can be cut, forged, and worked with as much ease as ordinary wrought iron.

The tempering of steel is an operation of great practical importance, as from the variety of purposes to which it is applied, it is required of very different degrees of hardness, and upon the due adjustment of this quality much of its utility depends. The degree to which the temperature is raised in the second heating, regulates this point: the higher the heat, the softer is the steel. In practice, the workman judges with sufficient accuracy of the temperature to which the metal has been exposed, by observing the colour which the steel assumes owing to the varying thickness of the film of oxide which is formed upon its surface.

The first perceptible tint is a light straw colour, which is produced by the lowest degree of heat, and indicates the hardest temper; the heat required is from 220° to 230° (428° to 446° F.); it is used for tools employed in cutting iron, and for lancets, razors, and surgical instruments: at 232°2 (450° F.), a straw yellow tint appears; this steel is used for drills, and for tools for working brass: at 245° (480° F.), a full yellow is produced: it is the temper fitted for scapels, penknives, and fine cutlery. The temperature of 255° (491° F.) gives a brown yellow, which is the temper for scissors, stonemason's tools, and shears intended for cutting iron. At 265° (509° F.) the first tinge of purple shows itself: this is the temper employed for pocket-knives; 270° (518° F.) gives a purple, which is the tint for table and carving knives. A temperature of from 280° to 300° (536° to 572° F.) produces various shades of blue, such as are

used for axes, watch-springs, sword-blades, saws, needles, and instruments requiring great elasticity. The different degrees of heat may be exactly regulated by heating the different articles in a fusible metal- or oil-bath, the temperature of which is ascertained by means of thermometers, although in ordinary cases this degree of nicety is not observed. The following table gives the composition of alloys and their fusing points:

Colour.	Temperature °C.	Temperature °F.	Alloy of tin and lead.
Pale straw ...	215·5	420	7 lead 4 tin
Straw	232·2	450	8
Deep straw ...	294·0	480	8½
Nut brown ...	260·0	500	14
Purple	276·6	530	19
Bright blue ...	304·5	580	48
Deep blue ...	310·0	590	50
Very deep blue	337·7 *	640	all lead*

For some purposes, as engraver's plates and mild steel boiler plates, it is desirable to have the steel as soft as possible, and for this purpose it is annealed by heating it to redness, and cooling very slowly. On the large scale this is done by packing the steel in iron boxes with lime, then heating, and allowing them to cool very slowly during several days.

Hardened steel is somewhat less dense than wrought steel. It appears that a portion of the carbon contained in steel, before the alloy has been hardened, is in the uncombined state; this portion is left in the form of graphitic scales when the metal is dissolved in hydrochloric acid: but after the steel has been hardened, the whole of the carbon is chemically united with the iron; so that, when treated with acids, it is separated in the form of a hydrocarbon, which causes the solution to have a dark colour. Eggertz has taken advantage of this for the determination of the amount of carbon in steel by a rapid colorometric process which is exceedingly valuable for testing Bessemer steel. Before it has been hardened steel may be worked as easily as iron, and in certain cases may be welded upon that metal. Instruments are completely finished in the soft state, and are then hardened and subsequently tempered.

It is sometimes desirable, as in axles, shaft bearings, lathe mandrils, &c., to combine the toughness of soft iron with the hardness of steel by converting the articles manufactured from soft iron superficially into steel. This is termed *case-hardening*, and is effected by heating them for a comparatively short time in contact with powdered cast-iron turnings, or powdered charcoal; or still better, with horn shavings, leather cuttings, hoof parings,

* Boiling linseed oil gives the same blue-black tint.

or bone dust. The same object is attained if they are sprinkled, when red hot, with powdered potassic ferrocyanide.

(848) **Preparation of Pure Iron.**—In order to obtain iron chemically pure, Berzelius recommends that filings of the best bar iron be intimately mixed with one-fifth of their weight of pure ferric oxide, and placed in a Hessian crucible, covered with pounded glass (free from lead); the cover is then to be carefully luted on, and the crucible to be exposed for an hour to the strongest heat of a smith's forge. By this means, all traces of carbon and of silicon are oxidized at the expense of the oxygen of the ferric oxide, whilst the excess of oxide forms a fusible slag with the glass. If the operation be successful, the iron will be melted into a button, with a lustre approaching that of silver. Such iron is very tough, and much softer than ordinary bar iron: it has a density of 7·8439. Pure iron may also be obtained in the state of fine powder, by decomposing the pure sesquioxide at a red heat in a current of hydrogen gas. Iron has been obtained in hollow tetrahedra, apparently belonging to the cubic system, by reducing ferrous chloride in a current of pure hydrogen. It may be deposited in flexible laminæ from a mixed solution of ferrous chloride and ammonic chloride, by the action of the voltaic current; it then has a density of 8·1393. According to Stahlschmidt pure iron of a silvery lustre and soft enough to be cut with a knife may be obtained by heating nitride of iron in a current of hydrogen. It was found to be of density 6·03.

(849) **Properties of Bar Iron.**—The bar iron of commerce is never pure. It always retains small quantities of carbon, varying from 0·2 to 0·4 per cent., and traces of silicon and sulphur; occasionally, also of phosphorus and arsenicum. The presence of this small quantity of carbon much increases its hardness and tenacity, but the other ingredients act injuriously upon the metal.

Bar iron has a bluish-white or grey colour, and is endowed with considerable lustre and hardness; it takes a high polish: its texture is usually fibrous, and when broken across it exhibits a ragged or hackly fracture; when rubbed, it emits a peculiar characteristic odour. The average density of good bar iron is 7·7. It requires the most intense heat of a wind furnace for its fusion, but passes through a soft pasty condition before it is completely melted; this property is one of great practical importance, for if two pieces of iron be heated to whiteness, sprinkled with sand, and hammered together, they may be united or *welded* so completely, that the junction is as tough as any other part of the

metal. The sand is used as a flux to the oxide of iron, with which it forms a slag which coats each piece of the metal; by the blow of the hammer this layer of melted matter is forced out, and the two clean surfaces of metal become united together. At a red heat, iron may be forged into any shape with facility, although at ordinary temperatures it possesses but little malleability as compared with gold and silver. It however admits of being rolled into very thin sheets. In ductility, iron stands very high in the scale, and in tenacity it far exceeds all other known substances, with the exception of cobalt and nickel.

If compared with other metals, iron is inferior to many of them as a conductor of heat and of electricity. Its susceptibility to magnetism is peculiar, no other metal exhibiting this property in any marked degree, excepting cobalt and nickel, and in them the power is developed to a much smaller extent. But although iron in its pure state is susceptible of magnetic induction, it cannot be permanently magnetized unless it be combined with carbon, as in steel, with oxygen, as in the loadstone, Fe_3O_4, or with sulphur, as in certain varieties of pyrites, Fe_3S_4, and Fe_7S_8. It is especially worthy of observation, that if oxygen or sulphur be present in quantity either greater or less than in these particular compounds, not only is the power of retaining magnetism destroyed, but the mass becomes almost indifferent to the action of a magnet. Iron loses nearly all its magnetic power when heated to redness, but recovers it again on cooling.

At a high temperature, iron burns readily, emitting vivid scintillations, as may be seen at the blacksmith's forge, or still more brilliantly when a glowing wire is introduced into a jar of oxygen. In a very finely divided state, such as that produced by reducing precipitated ferric oxide at a low temperature in a current of hydrogen, the metal takes fire by mere exposure to the atmosphere. If a small quantity of alumina be precipitated with the ferric oxide, so as to interpose some foreign matter between the particles of the metal, this pyrophoric property is much increased. A polished mass of the metal, however, preserves its lustre unchanged in dry air at ordinary temperatures for an unlimited time, but when exposed to a moist atmosphere, so that water in the liquid form shall be deposited upon the metal, its surface is quickly altered, and it becomes covered with rust. When once a spot of rust begins to show itself, the oxidation proceeds rapidly: moisture is absorbed from the air by the oxide, and thus a species of voltaic action is produced, the oxide performing the part of an electronegative element, whilst the iron

becomes electropositive, and the atmospheric moisture acts as the exciting liquid. The carbonic acid derived from the air contributes in an important way towards increasing the rapidity with which this change occurs, and according to Calvert it is indispensable, since he finds that iron does not rust in perfectly pure water; alkaline hydrates and carbonates also prevent the oxidation. It appears that hydrated ferrous carbonate is first formed; this is afterwards decomposed by the further absorption of oxygen, being converted into the hydrated sesquioxide, or rust of iron, whilst the liberated carbonic acid forms a fresh portion of ferrous carbonate: a portion of water is deoxidized in the process, and hydrogen is evolved; if a considerable heap of iron turnings be moistened and exposed to air, the peculiar odour of hydrogen, as evolved from a metallic carbide, is perceived, and the temperature of the mass rises considerably. Iron rust always contains ammonia, derived probably from the reaction of the nascent hydrogen of the water upon the nitrogen of the atmosphere, which is dissolved in the water with which the metal is moistened. Even the native oxides of iron invariably contain traces of ammonia (Chevallier). Iron may be kept for any length of time in water quite free from air without undergoing change, as well as in lime-water, or in water containing a little caustic or carbonated alkali, but the alkaline bicarbonates do not exert this protective action. At a red heat iron decomposes water rapidly, and liberates hydrogen (340), whilst the iron is converted into minute crystals of the black or magnetic oxide; the following equation illustrates the chemical change: $4OH_2+3Fe=4H_2+Fe_3O_4$.

Chlorine, bromine, and iodine combine quickly with iron, and dissolve it easily at ordinary temperatures, if the metal be digested with them in presence of water. Iron is soluble in dilute sulphuric and hydrochloric acids, with evolution of hydrogen, a portion of the gas appearing to be dissolved or occluded by the metal (O. Reynolds, *Chem. News*, 1874, xxix. 118). Even carbonic acid, when contained in water from which air is excluded, slowly dissolves this metal with evolution of hydrogen, and the ferrous carbonate formed is dissolved in the excess of carbonic acid. Concentrated sulphuric acid has but very little action on iron, even when boiled with it—a slow solution, attended with the evolution of sulphurous anhydride, occurring: but the metal is rapidly attacked by nitric acid, with abundant evolution of nitric oxide.

(850) **Passive Condition of Iron.**—Under certain circumstances iron may be kept in concentrated nitric acid for weeks, without the slightest action,

or alteration of the polish of its surface. There are various methods of producing this *passive condition* of iron in an acid of a moderate degree of concentration; some of these seem to indicate an intimate connexion with its voltaic relations. This will be rendered evident from the following statement of some of the circumstances under which this remarkable phenomenon is manifested:—If a piece of clean iron wire be introduced into nitric acid of a density of about 1·35, immediate and brisk action ensues; but if the metal be touched beneath the surface of the liquid with a piece of gold, of platinum, or of plumbago, the chemical action, contrary to what might have been anticipated, is suddenly arrested if the temperature of the acid has not been allowed to rise too high. If a second iron wire be made to touch the first, and then be introduced into the acid, it also is rendered inactive. This second wire may be used in like manner to render a third inactive. But if any of these inactive wires be withdrawn from the acid, and exposed to the air for a few seconds, it will be found to be rapidly acted on upon again introducing it into the acid. If, whilst in the acid, the iron wire be made the zincode of a voltaic arrangement, oxygen gas is evolved from the surface of the iron, but does not combine with it. If, on the contrary, a piece of passive iron be made the platinode or negative plate of the arrangement, it is immediately attacked by the acid.

By heating the end of a clean iron wire in the flame of a spirit-lamp so as to give it a superficial coating of oxide, the wire is brought into the passive condition.* If into acid containing a passive wire, a second ordinary wire, not in contact with the first, be introduced, brisk action on the ordinary wire ensues; and on causing the passive wire to touch the active one, action immediately occurs on both. Clean iron wire exposed to nitrous vapours for 10 minutes or more is also rendered passive.

Strong nitric acid, of density 1·45, renders all iron passive; the metal may be kept in it for years without losing its brilliancy or showing any action; and a wire withdrawn from the strong acid and plunged into acid of 1·35, still remains passive. If it be wiped first, and then plunged into the weaker acid, it immediately begins to be dissolved. If the acid be diluted below a density of 1·35, it dissolves the metal rapidly, whatever may have been its previous condition. It appears, moreover, that for each strength of the nitric acid employed there is a particular temperature below which the iron is rendered passive, but above which it has no such action. For many interesting particulars concerning the passive state of iron the papers of Renard (*Compt. Rend.*, 1874, lxxix. 159 and 508), and De Regnon, (*ibid.*, lxxix. 299) may be consulted.

(851) **Alloys of Iron.**—Iron forms alloys with most of the metals; but they are not in general of much importance. The presence of small quantities of silver, copper, arsenicum, or sulphur in iron, is said to occasion a defective quality of metal, technically known as *red short*. Such iron is tough at ordinary temperatures, but becomes brittle when heated to redness for forging. The presence of a quantity of antimony not exceeding

* Similar effects are produced with wires of cobalt or of nickel, although with them the action is less strongly marked (Nicklès). Such wires, if placed in voltaic relation with an active wire of the same metal, are found to be strongly electronegative towards it; but passive iron, cobalt, and nickel are electropositive in relation to platinum. Andrews has shown that bismuth also may be rendered passive in concentrated nitric acid.

0·23 per cent., was found by Karsten to render it both cold short and red short.

The mode of preparing zinc-plate or galvanized iron has been already described (782). Tin-plate is prepared by an analogous process; it consists of iron superficially alloyed with tin (923).

(852) **HYDRIDE OF IRON.**—Wanklyn and Carius have described a compound of hydrogen with iron prepared by the action of ferrous iodide on zinc-ethyl. It has not been analysed, but is described as a black powder which evolves pure hydrogen when gently heated: hydrochloric acid dissolves it with evolution of hydrogen. Cailletet (*Compt. Rend.*, 1875, lxxx. 319), on decomposing a solution of ferrous chloride mixed with ammonic chloride, by the electric current, obtained metallic iron, which, when plunged into pure water or any other liquid, became covered with bubbles of hydrogen, the gas being given off rapidly on raising the temperature to 60° (140° F.). This iron was found to contain 240 times its volume of hydrogen. The occlusion of hydrogen by iron when acted on by dilute acids has already been referred to (p. 640).

(853) **FERROUS CHLORIDE,** *Protochloride of Iron,* $FeCl_2$= 127; *Density, anhydrous,* 2·528; *cryst.* 1·926.—Iron forms with chlorine two compounds, ferrous chloride, $FeCl_2$, and ferric chloride, $FeCl_6$, the former of which may be obtained in the anhydrous state by passing dry hydrochloric acid gas over ignited metallic iron: the acid is thereby decomposed, hydrogen gas escapes, whilst the chlorine combines with the iron, and the white ferrous chloride sublimes at a temperature at which glass begins to soften; it can also be readily prepared by heating ferric chloride in a current of hydrogen. It may be obtained in solution by dissolving iron in hydrochloric acid; the hot, saturated liquid deposits the salt, on cooling, in green hydrated crystals, $FeCl_2.4OH_2$. It is very soluble in water, and is taken up in considerable quantity by alcohol. If heated in the open air, chlorine escapes and ferric oxide remains.

Ferrous chloride unites with ammonic chloride, and forms a double salt, from which the iron may be deposited upon various metallic articles, by boiling them in this solution with scraps of zinc; the zinc displaces the iron, which is deposited in a coherent lamina upon the other metals, in consequence of voltaic action.

(854) **FERRIC CHLORIDE,** *Sesquichloride* or *Perchloride of iron,* Fe_2Cl_6=325; *Theoretic Density of Vapour,* 11·245; *Observed,* 11·39; *Mol. Vol.* [ ]; *Rel. wt.* 162·5.—This compound sublimes in lustrous brown scales when dry chlorine is passed over iron heated to redness. The anhydrous chloride is very deliquescent, and hisses when thrown into water, forming a red solution. It is also soluble both in alcohol and ether. In a

hydrated condition it may be procured by evaporating a solution of ferrous chloride through which chlorine has been passed to saturation, or by dissolving hydrated ferric oxide in hydrochloric acid: the solution, by concentration, yields red deliquescent rhombic plates, $Fe_2Cl_6.6OH_2$, but the salt cannot be rendered anhydrous by evaporation, as it is decomposed into hydrochloric acid and ferric oxide. It also crystallizes with $10OH_2$ and $12OH_2$, the latter being stellate, orange-coloured groups, which are less deliquescent than the other hydrates. Crude ferric chloride is sometimes used in solution as a disinfectant: it deodorizes sewerage products quickly, and is partially reduced to the condition of ferrous chloride. Ferric chloride forms a double salt with ammonic chloride, which crystallizes readily in cubes, and is known in pharmacy as the *ammonio-chloride of iron*. The composition of this salt varies considerably; it is of a ruby-red colour, and seldom contains more than 2 per cent. of iron. Double salts of ferric chloride with sodic chloride and with potassic chloride may also be formed.

A hydrated *ferric oxychloride* is formed when a solution of ferrous chloride is exposed to the air, or when ferric chloride is precipitated by a small quantity of caustic alkali. It is insoluble in water containing salts, but is partially soluble in pure water.

(855) **BROMIDES OF IRON.**—These correspond in composition to the chlorides. *Ferrous bromide*, $FeBr_2$, is a yellow compound, obtained in the anhydrous state by passing bromine vapour over heated iron wire, or in crystals of the hydrate, $FeBr_2.6OH_2$, by evaporating a solution of the metal in hydrobromic acid. *Ferric bromide*, Fe_2Br_6, is a reddish-brown mass, which deliquesces on exposure to the air. It may be obtained by the action of excess of bromine on the ferrous salt.

(856) **FERROUS IODIDE**, or *Protiodide of iron*, $FeI_2=310$, is formed by digesting iron wire or filings, in a closed vessel, with four times their weight of iodine suspended in water: direct combination takes place between the elements, the iodide is dissolved and forms a pale green solution, which, by evaporation *in vacuo*, yields crystals containing $FeI_2.4OH_2$; density 2·873. By a continued heat it may be rendered anhydrous, and in that state is fusible. Its solution, if exposed to the air, absorbs oxygen and is decomposed; iodine is set free, and a hydrated ferric oxyiodide falls. This change is retarded by mixing the solution with strong syrup; and as the compound is employed in medicine, this method is frequently adopted to preserve unifor-

mity in its composition. No definite crystallizable *ferric iodide* is known.

FLUORIDES OF IRON.—Crystalline *ferrous fluoride*, FeF_2, and *ferric fluoride*, Fe_2F_6, have been prepared, the first by the action of aqueous hydrofluoric acid on metallic iron, the latter by dissolving ferric oxide in hydrofluoric acid.

(857) **OXIDES OF IRON.**—Iron yields four definite compounds with oxygen: 1. The *protoxide*, FeO, which is the base of the green, or ferrous salts of iron corresponding to ferrous chloride: 2. The *sesquioxide*, Fe_2O_3, which is the base of the red, or ferric salts corresponding to ferric chloride: 3. The black, or *magnetic oxide*, Fe_3O_4, which may be viewed as a compound of the two preceding oxides, or $FeO.Fe_2O_3$; it does not form any definite salts: 4. *Ferric acid*, the anhydride of which is unknown; it is a weak and unstable metallic acid, and as such it forms salts with the alkalies, like *potassic ferrate*, K_2FeO_4.

(858) **FERROUS OXIDE**; *Protoxide of iron*, FeO=72; *Comp. in* 100 *parts*, Fe, 77·78; O, 22·22.—It is obtained in the form of a white hydrate by dissolving a pure ferrous salt in water recently boiled, and precipitating it by an alkali, the solution of which has been similarly treated, both being allowed to cool out of contact with air, and being mixed in vessels from which air is excluded. If this precipitate be boiled in a vessel from which oxygen is excluded, it loses its water of hydration, like cupric oxide under similar circumstances. According to Tissandier (*Compt. Rend.*, 1872, lxxiv. 531), anhydrous ferrous oxide may be obtained in the crystalline state by heating pure iron to redness in an atmosphere of carbonic anhydride, the reaction being $Fe + CO_2 = FeO + CO$. Hydrated ferrous oxide absorbs oxygen from the air with avidity, passing through various shades of light green, bluish green, and black, until finally it assumes an ochry hue, due to the formation of the hydrated sesquioxide. It is insoluble in water, but is somewhat soluble in ammonia; this solution quickly absorbs oxygen from the air, and a film of insoluble ferric oxide is formed upon its surface. Ferrous oxide is readily dissolved by acids, and forms with them salts which are known as the *ferrous salts* or *protosalts of iron*; they have a green colour, and an astringent, inky taste. The solutions of these salts are decomposed when exposed to the air; gradually absorbing oxygen and becoming converted into ferric salts, which are partly retained in solution, and partly precipitated as a rusty coloured basic salt. For example, in the case of ferrous sulphate, the change may be represented as follows:

$$20Fe''SO_4 + 5O_2 + 6OH_2 = 6[(Fe''')_2 3SO_4] + 2(2Fe'''_2O_3.SO_3.3OH_2).$$

Ferrous sulphate. — Soluble ferric sulphate. — Insoluble ferric sulphate.

(859) **FERRIC OXIDE**; *Peroxide, Red oxide,* or *Sesquioxide of iron,* $Fe'''_2O_3 = 160$; *Comp. in* 100 *parts,* Fe, 70; O, 30.—The anhydrous sesquioxide is prepared for use in the arts by igniting the ferrous sulphate (871), and is known under the names of *colcothar, crocus of Mars,* or *rouge,* according to the degree of levigation to which it has been submitted; it is extensively employed for polishing glass, and by jewellers for putting a finish to their goods. It is also used as a red pigment.

The sesquioxide occurs native in great abundance; several of its varieties have been already mentioned as among the most valuable ores of iron. The specular ore of Elba (density 5·22) often presents natural facets of the most perfect polish, and of remarkable size and lustre. It occurs crystallized in forms of the rhombohedral system, and is isomorphous with alumina in corundum. Red hæmatite (density from 4·8 to 5·0), another of its varieties, is extremely hard, and, when polished, is employed for burnishing gilt trinkets.

Hydrates of Ferric Oxide.—There are several of these. Brown hæmatite is the hydrate, $2Fe_2O_3.3OH_2$, density 3·98. This mineral is readily dissolved by acids. It contains 59·89 per cent. of iron, with 25·67 of oxygen, and 14·44 of water. Another native hydrate, *göthite,* $Fe_2O_3.OH_2$, (density 4·12 to 4·37) has been found crystallized in prisms. Brown hæmatite gives the red and yellow colour to the different varieties of clay.

The sesquioxide is best obtained in a state of purity, by precipitating the ferric chloride by ammonia in excess. It falls as a bulky light-brown flocculent hydrate, which shrinks remarkably as it dries: if precipitated in a cold solution, and dried without heat over sulphuric acid, it contains $2Fe_2O_3.3OH_2$ (St. Gilles), but it is apt to retain a little ammonia, which is easily expelled by heat. The same hydrate is also formed when moist iron is allowed to become oxidized by exposure to air. If the hydrate be not dried, but allowed to remain for some months under water, it becomes crystalline, and according to Wittstein, is converted into an allotropic hydrate ($2Fe_2O_3.3OH_2$?), but if dried at 100° (212° F.), it retains 10·11 per cent. of water, corresponding in composition to $Fe_2O_3.OH_2$. A hydrate having the composition, $Fe_2O_3.2OH_2$, is also known. Hydrated ferric oxide slowly parts with its water at a prolonged heat of 320° (608 F.), and if subsequently heated to dull redness, it suddenly contracts in bulk, and glows brightly for a few moments whilst undergoing molecular change; after this it is dissolved by acids with difficulty, but is more readily attacked by a solution of ferrous chloride in hydrochloric acid: at a very high temperature the sesquioxide loses one-ninth of its oxygen, and is converted into the magnetic oxide of iron.

Hydrated ferric oxide, when recently precipitated from cold solutions, is easily soluble in acids, forming the *persalts of iron,*

or *ferric salts*; they have a strongly acid reaction, and are not, as a rule, crystallizable: many of them are deliquescent. Their concentrated solutions have the property of dissolving a considerable excess of the oxide, in which case they assume a deep red colour. If these basic solutions be diluted and boiled, the iron is entirely separated in the form of an insoluble ferric subsalt.

If well washed and freshly precipitated hydrated ferric oxide, obtained by the action of ammonia upon ferric chloride in the cold, be boiled in water for a few minutes, it becomes converted into the hydrate, $Fe_2O_3.OH_2$; but if the ebullition be continued for 8 or 10 hours, its colour becomes changed from ochry brown to brick red, and it is converted into an allotropic modification of the same hydrate, and by prolonged boiling, a portion of it even loses all its water. This modified oxide is insoluble in strong boiling nitric acid, and only slowly soluble in hot hydrochloric acid. Cold acetic acid, and cold dilute hydrochloric and nitric acids dissolve it, forming a red liquid which appears to be turbid by reflected light; concentrated nitric or hydrochloric acid occasions a red precipitate in this solution, but it becomes redissolved on the addition of water. The solution is also precipitated by the addition of any sulphate, or of any salts of the alkali-metals. If the ordinary hydrated ferric oxide be kept long in water, especially if at the same time it be exposed to a low temperature, it experiences a similar modification in composition and properties. An acetic solution of this oxide, if kept for some time in a closed vessel at 100° (212° F.), becomes of a brighter red colour. It appears to be turbid when viewed by reflected light, but clear by transmitted light. It has lost its astringent metallic taste. The addition of a soluble sulphate causes an immediate precipitate, and so do the strong acids: it is no longer reddened by the addition of a sulphocyanide, and does not give a precipitate of Prussian blue with potassic ferrocyanide (Péan de St. Gilles, *Ann. Chim. Phys.*, 1856, [3], xlvi. 47). Graham found that if a solution of ferric chloride, in which a large quantity of hydrated ferric oxide had been dissolved by prolonged digestion in the cold, were submitted to dialysis, a solution was eventually obtained which contained a proportion of 98·5 of the oxide and 1·5 of hydrochloric acid. This solution, however, in a few weeks became spontaneously gelatinous in the bottle to which it was transferred.

Hydrated ferric oxide is now used to a large extent for the purpose of purifying coal-gas from sulphuretted hydrogen, which is always produced during the distillation of coal. For this purpose the oxide is mixed with sawdust, and placed in layers of 10 or 12 inches (25 or 30 cm.) in thickness, upon the perforated shelves of a dry lime purifier: hydrated ferric sesquisulphide and water are formed; $Fe_2O_3.xOH_2 + 3SH_2 = Fe_2S_3.xOH_2 + 3OH_2$. After the mixture has ceased to absorb any more sulphuretted hydrogen, it is oxidized by exposure to a current of air; hydrated ferric oxide is thus reproduced, and sulphur is set free; $2Fe_2S_3.xOH_2 + 3O_2 = 2Fe_2O_3.xOH_2 + 3S_2$. The mixture may again be used for the same purpose as at first, and this process may be repeated several times in succession, until the accumulation of sulphur mechanically impairs the absorbent powers of the mixture. Considerable elevation of temperature attends the act

of reoxidation, which must therefore be prevented from taking place with too great rapidity.

Ferric oxide combines with some of the more powerful bases, towards which it acts the part of a feeble acid. The compounds which it forms by heating it with potassic and sodic hydrates are easily decomposed by water, but the oxide retains traces of these bases with great obstinacy. According to Pelouze, when 4 molecules of lime and 1 molecule of ferric oxide are precipitated together and boiled, they unite and form a white compound, $4CaO.Fe_2O_3$, which is readily decomposed by the feeblest acids. Ferric oxide occurs native combined with zincic oxide in crystals, mixed with oxide of manganese, constituting *Franklinite.* With ferrous oxide it forms the black or magnetic oxide of iron.

(860) **MAGNETIC IRON OXIDE,** or *Black oxide of iron,* Fe_3O_4; *Density,* 5·09; *Comp. in* 100 *parts,* Fe, 72·41; O, 27·59.—This oxide occurs as a well-known mineral, the *loadstone,* which acquires its magnetism from the inductive influence of the earth. It is found in primitive rocks, forming beds, or sometimes, as in Sweden, entire mountains. It furnishes a very pure and excellent iron, of which a large quantity is annually supplied from the Swedish and American mines. It has a black colour and metallic lustre; it crystallizes in cubes, octahedra, or rhombic dodecahedra. Magnetic oxide of iron is the principal constituent of the scales of oxide which are detached during the forging of wrought iron. It fuses at a high temperature, and is formed when iron is burned in oxygen. The magnetic oxide is also formed by passing steam over heated iron turnings, and Barff has recently applied this to the preservation of iron, the thin coating of magnetic oxide serving to protect the iron from further oxidation. A hydrate of this oxide, $Fe_3O_4.OH_2$, may be prepared by dividing a freshly prepared solution of ferrous sulphate into three equal portions: two of these are acidulated with sulphuric acid and heated to the boiling-point; to the boiling liquid nitric acid is added gradually as long as its addition causes the evolution of nitric oxide: when this point is reached, the whole of the ferrous salt will have been converted into a ferric salt; $6Fe''SO_4+3H_2SO_4+2HNO_3=3Fe'''_2SO_4+N_2O_2+4OH_2$: the remaining portion of the solution of the ferrous sulphate is then poured into the hot liquid, and sodic carbonate or ammonia solution is added in slight excess: the solution and precipitate are boiled together, and the black oxide is formed as a heavy crystalline powder. The magnetic oxide is soluble without difficulty in hydrochloric acid, as well as in nitric acid and in aqua regia: this oxide, however, when treated with acids does not form specific salts, but mixtures of ferrous and ferric salts; for example, $Fe_3O_4+4H_2SO_4=Fe''SO_4+Fe'''_2SO_4+4OH_2$.

If recently precipitated hydrated ferric oxide, obtained from ferric chloride by ammonia, be well washed, and without being dried be boiled with water and iron turnings in large excess, hydrogen is evolved, and magnetic oxide of iron formed.

(861) **FERRIC ACID,** $H_2FeO_4 = 122$.—If a mixture of 1 part of ferric oxide and 4 parts of nitre be heated to full redness for some time, a brown mass is obtained, which with water gives a beautiful violet-coloured solution, due to the presence of potassic ferrate: in this compound the iron is combined with a larger quantity of oxygen than in the sesquioxide, but the ferric anhydride itself has not been obtained in an isolated form. Potassic ferrate may be more easily prepared by suspending 1 part of recently precipitated hydrated ferric oxide in a concentrated solution of potassic hydrate, consisting of 30 parts of the hydrate and 50 of water, and passing a current of chlorine gas through the mixture; the potassic ferrate is insoluble in a concentrated solution of potash, and is deposited as a black powder, which may be drained upon a tile (Fremy). This compound is very soluble in water, but is precipitated in black flocks by a large excess of alkali. It is a very unstable salt, which in dilute solutions decomposes spontaneously; the alkali becomes free, hydrated ferric oxide subsides, and oxygen is evolved. Organic matter decomposes it speedily, just as it does potassic permanganate: a temperature of 100° (212° F.) destroys it instantly if in solution, and the addition of an acid, even in quantity insufficient to neutralize the whole of the alkali, causes the immediate separation of oxygen, and precipitation of ferric oxide.

Baric, strontic, and calcic ferrates may be obtained in the form of red insoluble precipitates, by mixing solutions of the salts of the earths with a solution of potassic ferrate.

(862) **NITRIDES OF IRON.**—When iron wire is heated in a current of dry ammoniacal gas for some hours it becomes brittle, but does not usually gain in weight more than about 0·2 per cent. Despretz, however, obtained a compound of iron with nitrogen in which 100 parts of iron increased to 111·5, becoming less dense, brittle, whitish, and less oxidizable than pure iron. Sulphuric acid easily dissolves this nitride with evolution both of hydrogen and nitrogen, whilst ammonic sulphate is retained in solution. Stahlschmidt prepares the nitride, Fe_4N_2, by strongly heating ferammonium chloride prepared by passing ammonia over ferrous chloride as long as it is absorbed: $4FeCl_2 + 4NH_3 = N_2Fe_4 + 8HCl + 2H_2 + N_2$. The compound obtained by Fremy by passing a current of dry ammonia over dried ferrous chloride heated to low redness in a porcelain tube is impure, since when nitride of iron is heated in a current of ammonia or of hydrogen it gives off its nitrogen. Silvester finds, however, that the nitride of iron from the lava of Etna has the same composition as that obtained by Fremy—namely, Fe_5N_2. If pure ferric oxide, as obtained from the oxalate by ignition, be heated in a current of ammonia, a brittle nitride is formed, consisting of Fe_3N (Rogostadius).

(863) **SILICIDE OF IRON.**—Iron combines in various proportions with silicon, furnishing a brittle, white, fusible, crystalline mass, which is but slowly attacked by hydrochloric acid. Hahn obtained a definite compound, Fe_2Si, of density 6·611, containing 20·3 per cent. of silicon, by fusing at a prolonged high temperature ferrous sodic chloride (obtained by fusing 40 parts of iron, 150 of sal ammoniac, and 80 of common salt) with a mixture of 5 parts of silicon, 25 of sodium, and 25 of fluor-spar.

It is probable that a compound, SiFe, also exists, as a very brittle silicide containing 30·86 per cent. of silicon has been obtained by Hahn, which is probably a mixture of Fe_2Si and FeSi, the latter requiring 33·3 per cent. silicon.

(864) **SULPHIDES OF IRON.**—Sulphur combines with iron in several proportions: the protosulphide, FeS, and the disulphide, FeS_2, are the most important; but besides these a subsulphide, Fe_2S, has been obtained by heating ferrous sulphate to redness in a current of hydrogen gas: a sesquisulphide, Fe_2S_3, may also be formed as a hydrate by precipitating the ferric salts by the protosulphides of the alkali-metals; and two magnetic sulphides of iron, Fe_7S_8, and Fe_3S_4, are found native.

(865) **FERROUS SULPHIDE,** *Protosulphide* or *Sulphuret of iron,* FeS=88, may be prepared by heating a bar of iron to whiteness and bringing it into contact with a roll of sulphur: immediate union takes place, and the resulting sulphide melts and runs down in drops of a reddish-brown colour: when formed in this manner it usually contains an excess of sulphur. It may also be prepared by projecting into a red-hot earthen crucible, in successive portions, a mixture of 7 parts of iron filings with 4 parts of sulphur in fine powder; vivid deflagration occurs at the moment of combination. Ferrous sulphide dissolves both iron and sulphur if either be present in excess; its composition, therefore, is variable. Like carbon, the presence of a minute portion of sulphur in wrought iron alters its quality, even $\frac{4}{10,000}$ of sulphur rendering it 'red short.' Anhydrous ferrous sulphide is dissolved by dilute sulphuric or hydrochloric acid with evolution of sulphuretted hydrogen; this decomposition is frequently employed in the laboratory as a convenient source of sulphuretted hydrogen. Aqua regia and concentrated nitric acid decompose it and form ferric nitrate or ferric chloride, setting part of the sulphur free, and converting the residue into sulphuric acid. When heated in the open air, this sulphide absorbs oxygen and becomes converted into ferrous sulphate; at a still higher temperature it is decomposed, sulphurous and sulphuric anhydrides escape, and ferric oxide remains.

Ferrous sulphide may be obtained as a black hydrate by precipitating a solution of a ferrous salt with a solution of a sulphhydrate of one of the alkali-metals; thus $2KHS + FeSO_4 + xOH_2 = FeS.xOH_2 + SH_2 + K_2SO_4$; in this condition it rapidly attracts oxygen from the air, and acquires a brownish-red colour, ferric oxide being formed and sulphur liberated. When iron is present in very minute quantities in a solution, and is precipitated by a

solution of ammonic sulphhydrate, the very finely divided particles of ferrous sulphide are apt to pass through the filter; the liquid then has a peculiar green tint.

If iron filings be mixed with two-thirds of their weight of sulphur in powder, and moistened, the mixture becomes hot when exposed to the air, and absorbs oxygen with sufficient rapidity to cause it in many cases to inflame; ferrous sulphide is at first formed, and this quickly becomes converted into sulphate. A valuable lute for the joints of iron vessels is composed of a mixture of 60 parts of iron filings sifted fine, and 2 of sal ammoniac in fine powder intimately blended with 1 part of flowers of sulphur. This powder is made into a paste with water, and applied immediately; in a few minutes it becomes hot, swells, disengages ammonia and sulphuretted hydrogen, and soon sets as hard as iron itself.

(866) **FERRIC DISULPHIDE**, or *Bisulphide of iron*, $FeS_2 = 120$; *Density*, 4·98; *Comp. in* 100 *parts*, Fe, 46·67; S, 53·33.—This compound is found abundantly in the native state, in two distinct forms—namely, as *Yellow iron pyrites*, or *Cubic pyrites*, and as *White iron pyrites* or *marcasite* crystallizing in right rhomboidal prisms. It occurs in the strata of every period: when found in the older formations it is crystallized in cubes, and sometimes in dodecahedra, of a brassy lustre, and is hard enough to strike fire with steel; but in the tertiary strata it occurs more frequently in fibrous radiated nodules. The formation of iron pyrites may occasionally be traced to the slow deoxidation of sulphates by organic matter in waters containing carbonate or other salts of iron in solution; it is then frequently deposited in cubes or octahedra. This appears to be the usual mode of its formation in alluvial soils. Some varieties of iron pyrites, especially those found in the tertiary strata, are speedily decomposed by exposure to air; oxygen is absorbed and ferrous sulphate formed. This decomposition occurs with greater facility if the disulphide be mixed with other substances, as is the case in the aluminous schists; in which by the further action of air, a basic ferric sulphate is formed, whilst the liberated sulphuric acid reacts upon the alumina, magnesia, or lime of the soil, and forms sulphates; those of aluminium and magnesium may be extracted by lixiviation. The ordinary crystallized pyrites from the older strata is not thus decomposed, but *marcasite* is rapidly disintegrated by exposure to the weather.

Iron pyrites is not acted upon by cold sulphuric or by hydrochloric acid, but is rapidly oxidized and dissolved by nitric acid and by aqua regia: boiling oil of vitriol dissolves it gradually with evolution of sulphurous anhydride. When heated in closed vessels it fuses, and sulphur is expelled. If heated in the air it

burns with flame, ferric oxide is formed, whilst sulphurous anhydride escapes in large quantity. This circumstance has been turned to account in the manufacture of oil of vitriol, for which purpose enormous quantities of *mundic*, as the disulphide is termed by the workmen, are annually consumed. The acid obtained from that source is usually contaminated with arsenic, which in small quantity is a common impurity of pyrites. Iron pyrites may be prepared artificially by exposing a mixture of powdered ferrous sulphide with half its weight of flowers of sulphur, in a covered crucible to a heat just below redness, as long as sulphurous fumes escape.

(867) **MAGNETIC IRON SULPHIDE**, Fe_7S_8; *Density*, 4·65.—This compound exhibits a brassy lustre, but is distinguished from ordinary pyrites by its solubility in hydrochloric acid. It is often formed artificially when sulphur and iron are heated together in preparing ferrous sulphide for use in the laboratory. Another variety of magnetic pyrites consists of Fe_9S_{10}.

(868) **A Potassic Ferric Sulphide**, $K_2Fe_2S_4$, has been obtained in purple-brown, flexible, shining needles by fusing one part of iron with 6 of potassic carbonate and 6 of sulphur, and extracting the fused mass with water. A sodic ferric sulphide, $Na_2Fe_2S_4.4OH_2$, has also been prepared.

(869) **Mispickel**, or arsenical pyrites, is an arsenide and sulphide of iron (FeSAs; *Density*, 6·13) which, amongst other localities, occurs abundantly in the Hartz, in Saxony, and in some of the Cornish mines; it crystallizes in right rhombic prisms, of a steel-grey colour and metallic lustre. When heated in closed vessels it is partially decomposed, and arsenious sulphide sublimes. If exposed to a high temperature in the open air, it produces ferric oxide, whilst arsenious and sulphurous anhydrides escape. Analogous compounds of cobalt and nickel occur amongst the ores of these metals.

Nitrosulphides of Iron.—A remarkable class of compounds, termed by Roussin, who discovered them, nitrosulphides of iron, may be obtained by the reaction of potassic nitrite and hydric ammonic sulphide upon the salts of iron: they form black needle-shaped crystals, to which he assigned the formula $Fe_3S_4(N_2O_2)_2SH_2$. This compound has more recently been examined by Porczinsky (*Ann. Chem. Pharm.*, 1863, cxxv. 302), who gives the formula $Fe_3S_3(N_2O_2)_2.2OH_2$; treated with potassic hydrate, it evolves ammonia, and the salt, $K_2S.Fe_2S_2(N_2O_2)_2$, is obtained in black triclinic crystals. Rosenberg (*Deut. chem. Ges. Ber.*, 1870, iii. 312) has also examined these bodies, but his results do not agree with those above given. At present the nature and composition of these bodies is far from satisfactorily settled.

(870) **DIFERROUS PHOSPHIDE**, Fe_2P, may be obtained by reducing the phosphate of the metal with charcoal: it fuses at a red heat, and forms an extremely hard, brittle mass, which unites with both phosphorus and iron in all proportions: its presence even in small quantity in bar iron appears to produce metal of the defective quality known as *cold short* iron.

TRIFERROUS PHOSPHIDE.—Schenck obtained a **Triferrous Phosphide**, Fe_3P_2, by adding a solution of ferrous sulphate to a boiling mixture of phosphorus with potassic hydrate solution, and continuing the boiling for some time. The compound is then thrown down as a black powder. Other phosphides of somewhat uncertain composition have been prepared by passing the vapour of phosphorus over heated iron.

(871) **FERROUS SULPHATE,** *Protosulphate of iron, Copperas,* or *Green vitriol,* $FeSO_4.7OH_2 = 152 + 126$; *Density, anhydrous,* 3·138, *cryst.* 1·857; *Comp. cryst. in* 100 *parts,* FeO, 25·90; SO_3, 28·78; OH_2, 45·32.—This salt is prepared in a state of purity by dissolving 1 part of pure iron, or 1½ of ferrous sulphide, by the aid of heat, in 1½ part of sulphuric acid diluted with 4 of water. The solution, quickly filtered, deposits on cooling beautiful transparent, bluish-green, rhomboidal crystals, with $7OH_2$. They effloresce in a dry air, and form a white crust, which soon becomes of a rusty-brown colour, owing to the absorption of oxygen, and formation of a basic ferric sulphate. If crystallized at a temperature of 80° (176° F.), the ferrous sulphate forms right rhombic prisms, which contain only $4OH_2$. It may also be obtained crystallized with 3, and with 2 molecules of water. For commercial purposes ferrous sulphate is formed by the decomposition of iron pyrites, or of aluminous schists containing pyrites, as already described when speaking of the manufacture of alum (736). The ferrous sulphate thus obtained has a grass-green colour, owing to the presence of a little ferric sulphate. Ferrous sulphate is largely used in combination with astringent vegetable matters as a black dye; ordinary writing-ink is a compound of this kind.

This salt is insoluble in alcohol, and requires twice its weight of cold water for solution. Its solubility is greater at 90° (194° F.) than at 100° (212° F.), 100 parts of water dissolving 370 parts of the crystals at 90° (194° F.) and only 333 at the boiling-point. This anomaly is probably dependent upon causes similar to those observed in the case of the sodic sulphate and carbonate. If exposed to the air, the solution absorbs oxygen, and a rusty-coloured basic ferric sulphate is precipitated, whilst normal ferric sulphate remains in solution; ultimately, however, the precipitate becomes richer in acid, approximating to the composition $2F_2O_3.3SO_3$, whilst the normal ferric sulphate loses acid, and a basic sulphate, $Fe_2O_3.2SO_3$, remains in solution. Owing to its strong attraction for oxygen, ferrous sulphate is occasionally used as a reducing agent: it is thus employed to precipitate gold and palladium in the metallic form from their solutions, and indigo is by its means brought into the soluble condition.

If heated gradually, each molecule of the crystallized sulphate loses 6 molecules of water and forms a white powder; 1 molecule of water being retained at all temperatures below 260° (500° F.). At a red heat the sulphate is decomposed; sulphuric anhydride is liberated, but one portion of the anhydride yields part of its oxygen to the iron, which is converted into the sesquioxide, whilst sulphurous anhydride escapes, $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$; but as in practice the salt cannot be rendered anhydrous in large quantities, a little water distils with the sulphuric anhydride, which is condensed as a brown fuming liquid, the 'Nordhausen sulphuric acid' (427). The residual ferric oxide is sold under the name of *colcothar* (859).

The aqueous solution of ferrous sulphate, in common with that of all the ferrous salts, has the power of absorbing a large quantity of nitric oxide, forming a deep brown solution which has a strong attraction for oxygen; if this solution be heated in closed vessels, the gas is for the most part expelled unchanged; if heated in air, nitric acid is formed in the liquid, and this converts the iron into a ferric salt.

With the sulphates of potassium and ammonium, green vitriol yields double salts precisely analogous in form and composition to those which are formed by these sulphates with cupric sulphate. The formula of the potassic salt is $FeSO_4.K_2SO_4.6OH_2$. The sodic salt, which is very stable and may be used for standardizing permanganate solution, has the formula $FeSO_4.Na_2SO_4.4OH_2$.

A *ferrous pyrosulphate*, FeS_2O_7, is obtained as a white crystalline powder on adding a large excess of concentrated sulphuric acid to a concentrated aqueous solution of ferrous sulphate, (Bolas).

(872) **FERRIC SULPHATE**; *Persulphate* or *Sesquisulphate of iron*, $Fe'''_2 3SO_4 = 400$.—This is made either by treating brown hæmatite with an excess of strong sulphuric acid, allowing it to digest for some time, and then expelling the excess of acid at a heat short of redness; or by mixing sulphuric acid and solution of ferrous sulphate in the proportion of one molecule of the former to two of the latter, boiling, and peroxidizing the iron by adding to the solution small quantities of nitric acid as long as any red fumes are given off. A yellowish-white deliquescent mass is obtained on evaporation, from which the acid is expelled by a red heat; at a more moderate heat, the salt is rendered anhydrous: water dissolves it but slowly. It is found native in large quantities in Chili as *coquimbite*, in the form of a white, silky, crystalline mineral consisting of six-sided pyramids, or of a white powder, $Fe'''_2 3SO_4.9OH_2$; and is sometimes deposited from its aqueous

solutions in crystals belonging apparently to the clinorhombic system. Several hydrated basic ferric sulphates may be obtained.

With potassic sulphate and the sulphates of the other alkali-metals, ferric sulphate forms double salts, resembling common alum in form and composition as well as in taste. The potassic salt, $K_3Fe'''_24SO_4.24OH_2$, is astringent, very soluble in water, but insoluble in alcohol: it is very prone to spontaneous decomposition, and becomes converted from a colourless transparent crystal into a brown, gummy, deliquescent mass: this change is also produced by heating the salt to a temperature below 100° (212° F.). The mixed solutions of the two sulphates should therefore be allowed to evaporate spontaneously during the preparation of this salt. The double salt with ammonium $(NH_4)_2Fe'''_24SO_4.24OH_2$, *density* 1·718, is much more permanent, and crystallizes readily in beautiful octahedra.

(873) **FERROUS NITRATE**; $Fe2NO_3.6OH_2 = 180 + 108$.—This salt may be obtained by dissolving ferrous sulphide in cold nitric acid of a density less than 1·12. Sulphuretted hydrogen is evolved in abundance, and on evaporating the solution *in vacuo* over oil of vitriol, it crystallizes in pale green rhombohedra, which when heated evolve nitric oxide, and yield a basic ferric nitrate; $6Fe2NO_3 = N_2O_2 + 3Fe_2O_3.5N_2O_5$. This change sometimes occurs spontaneously in warm weather. The basic salt is then freely soluble in water, and is not decomposed by ebullition. Ferrous nitrate may also be prepared by decomposing a solution of ferrous sulphate by an equivalent quantity of baric nitrate. It cannot be obtained in a pure form by treating iron with dilute nitric acid; since in that case the metal is dissolved without evolution of gas, and ammonia is formed in the liquid: $10HNO_3 + 4Fe = 4Fe2NO_3 + NH_4NO_3 + 3OH_2$.

(874) **FERRIC NITRATE**; $Fe'''_26NO_3.12OH_2$.—When nitric acid of density 1·2 or 1·3 is digested with metallic iron, a violent action occurs attended with the evolution of nitrous anhydride and of nitric oxide; the iron is at the same time converted into ferric nitrate, which is obtained with difficulty on evaporation in cubic crystals, if the solution contains one molecule of the crystallized salt and two of the hydrate of nitric acid, $HNO_3.OH_2$. Another salt containing $18OH_2$ has also been prepared.

(875) **FERROUS CARBONATE**, or *Protocarbonate of iron*, $FeCO_3 = 116$; *Comp. in* 100 parts, Fe, 48·27, or FeO, 62·07; CO_2, 37·93.—This substance is found native in immense quantities, forming a valuable ore of iron. In its less usual condition, when crystallized, it constitutes spathic iron ore, and occurs in yellowish lenticular crystals, the primary form of which is a rhombohedron, isomorphous with calcareous spar. The native carbonate very often contains manganous carbonate. The clay-iron ore, from which the greater part of the English iron is obtained, is, as already mentioned, an impure ferrous carbonate. Clay ironstone, besides the more usual form of bands or seams

accompanying the coal strata, occurs also in detached nodules or lumps, sometimes of very large size, imbedded in the clay of the same formations. When ferrous carbonate is strongly heated in vessels from which the air is excluded, carbonic anhydride and carbonic oxide are expelled, and magnetic oxide of iron is left, the decomposition being as follows: $3FeCO_3 = Fe_3O_4 + 2CO_2 + CO$. Ferrous carbonate is the salt contained in most ferruginous springs, in which it is held in solution by free carbonic acid: it is rarely present in a larger quantity than 1 grain per pint. Mere exposure to air causes its separation; the acid escapes, oxygen is absorbed, and hydrated ferric oxide, mixed with a small quantity of organic matter, subsides, forming the ochry deposits so usual around chalybeate springs. Ferrous carbonate may be produced artificially by mixing a ferrous salt with a carbonate of one of the alkali-metals, when it falls as a pale green voluminous hydrate which is speedily altered by exposure to air; it absorbs oxygen rapidly, losing its carbonic acid and becoming converted into the red hydrated sesquioxide: during the process of drying it is therefore almost completely decomposed. No stable ferric carbonate exists, but the hydric potassic and the hydric sodic carbonates dissolve hydrated ferric oxide; the red solution thus formed is very slowly decomposed by prolonged ebullition.

(876) **PHOSPHATES OF IRON.**—*Ferrous hydric phosphate*, $Fe''HPO_4$, falls as a white powder on adding trisodic phosphate to a ferrous salt; by exposure to air it absorbs oxygen, and becomes blue. A hydrated blue phosphate of iron is found native; it is known as *vivianite*. It is probably a mixture of ferrous and ferric phosphates, $Fe''HPO_4.Fe'''_2P_2O_8$, and contains in addition $8OH_2$, or about 30 per cent. of water.

A *ferric phosphate*, $Fe'''_2P_2O_8.4OH_2$, is obtained as a white powder by decomposing ferric chloride by an alkaline orthophosphate. Exposure of this salt to air produces no change. It is nearly insoluble in acetic acid, but somewhat soluble in ferric acetate: phosphoric acid is sometimes precipitated in this form in the course of analysis. Its composition varies according as the sodic phosphate or the ferric salt is in excess: other ferric phosphates have also been obtained (comp. Millot, *Compt. Rend.*, 1876, lxxxii. 89).

(877) **SILICATES OF IRON.**—Several native silicates of iron are known, but they are not important. The 'finery slag' obtained in the conversion of cast into wrought iron consists chiefly of ferrous orthosilicate, $2FeO.SiO_2$. Oxide of iron rapidly attacks clay crucibles if fused in them.

(878) **Characters of the Salts of Iron.**—Iron forms two classes of salts, both of which are readily distinguished from each other and from those of other metals. The salts of iron are not poisonous, unless administered in excessive quantities; they form valuable tonics and astringents when taken internally.

The solutions both of the ferrous and of the ferric salts have an inky, astringent taste.

1. *Ferrous salts,* or *Salts of the protoxide.*—These salts, when in solution, or when crystallized, have a pale green colour; they redden litmus, but very feebly. The addition of an *alkaline hydrate* to solutions of these salts causes a grey or green precipitate of hydrated protoxide, which on exposure to the air passes quickly through various shades of green into brown; this change of colour is due to the absorption of oxygen, in consequence of which the sesquioxide is eventually formed. If the precipitate be produced by *ammonia,* an excess of this reagent redissolves a part of the precipitate; and if the solution contains ammonic chloride, the whole of the oxide will remain dissolved: this solution absorbs oxygen rapidly from the air, and a film of ferric oxide is formed upon the surface. Ferrous salts of the mineral acids are not precipitated by *sulphuretted hydrogen* in solutions which are acidified with a mineral acid; but they give a black precipitate of hydrated sulphide on adding *ammonic hydric sulphide. Potassic ferrocyanide* (or yellow prussiate), gives a pale blue precipitate, which, on exposure to the air, deepens in tint, owing to the absorption of oxygen. *Potassic ferricyanide* (or red prussiate), when added to a neutral or acid solution, gives a bright blue precipitate, which is one of the varieties of Prussian blue, $Fe_3Fe_2Cy_{12}.xOH_2$. If a solution of a ferrous salt be boiled with *nitric acid,* the metal is completely converted into a ferric salt: the same effect is produced by chlorine or bromine, or by boiling an acidulated solution of the salt with a small quantity of potassic chlorate.

2. *Ferric salts,* or *Persalts,* or *Salts of the peroxide.*—In solution, they have a yellow or reddish-brown colour. *Hydrosulphuric acid* reduces them to the state of ferrous salts, whilst a white deposit of sulphur occurs: for example, with ferric sulphate the following reaction takes place: $2Fe'''_23SO_4+2SH_2=4Fe''SO_4+2H_2SO_4+S_2$. With *ammonic hydric sulphide,* a black hydrated ferric sesquisulphide is precipitated. The *alkaline hydrates* give a voluminous reddish-brown precipitate of hydrated sesquioxide, insoluble in excess of the alkali. *Potassic sulphocyanide* in neutral or acid solutions gives an intensely blood-red solution: *potassic ferrocyanide,* a bright blue precipitate of Prussian blue, $Fe_43FeCy_6.xOH_2$. *Potassic ferrocyanide* occasions no precipitate in solutions of the ferric salts, but the liquid acquires a greenish hue; the ferric salts may thus be distinguished from the ferrous salts. *Tincture of galls,* in neutral solutions, yield a bluish-black,

inky precipitate; it is the colouring matter of ordinary writing-ink; this test is rendered much more delicate in its indications by the addition of water holding a little calcic carbonate in solution in carbonic acid. In neutral solutions the *benzoates* and the *succinates* of the alkali-metals give voluminous insoluble precipitates: benzoate or succinate of ammonium or potassium has been employed to separate iron from nickel and cobalt, as the benzoates and the succinates of these metals are soluble. If a solution of a ferric salt, to which an alkali has been added until it begins to occasion a permanent precipitate, be raised to the boiling-point, it is completely decomposed, and an insoluble basic ferric salt is precipitated: this property is often turned to account in the separation of iron from cobalt, nickel, and manganese, which are not precipitated under similar circumstances. When a ferric salt in solution is digested with a bar of zinc in a flask provided with a tube for the escape of the gas, the zinc is dissolved with evolution of hydrogen, forming a zinc salt, whilst the whole of the iron is precipitated as sesquioxide.

Before the blowpipe both classes of the salts of iron act alike: in the reducing flame they give a green glass with borax, which becomes colourless, or yellowish (if the iron be in large quantity) when held in the oxidizing flame.

(879) **Estimation of Iron.**—In estimating the quantity of iron for the purposes of analysis, it should be first converted into a ferric salt, by boiling with nitric acid, after which it may be precipitated by excess of ammonia, and then well washed and ignited: pure ferric oxide remains, consisting, in 100 parts, of 70 of iron and 30 of oxygen. Iron is thus readily separated from the alkalies and alkaline earths. If magnesia be present, it is apt to be partially precipitated with the ferric oxide, unless the solution contains a considerable quantity of ammonic chloride. In the presence of tartaric acid, sugar, and some other organic substances, ammonia precipitates the ferric oxide but very imperfectly; in such cases ammonic hydric sulphide should be employed, which completely precipitates the iron as sulphide: this precipitate must be redissolved in nitric acid, and the iron may then be obtained as sesquioxide by adding excess of ammonia to the solution.

(880) **Separation of Iron from Aluminium and Glucinum.**—If alumina and glucina are contained in the liquid, they are precipitated along with the ferric oxide on the addition of ammonia. When these earths are present, the precipitation should be effected by an excess of potassic hydrate instead of by ammonia, and the precipitate should be gently warmed with the liquid, for

the purpose of dissolving out the earths. The solution is to be filtered from the ferric oxide, which requires long washing with boiling water to remove the last traces of potash. The alumina and glucina are obtained from the alkaline filtrate by neutralizing it with hydrochloric acid, and then adding a slight excess of ammonia; hydrated alumina and glucina are precipitated together, and must be separated in the manner already described (749). An elaborate paper on the quantitative separation of iron, aluminium, and phosphoric acid, by W. Flight, will be found in the *Jour. Chem. Soc.*, 1875, xxviii. 592.

(881) **Separation of Iron from Zinc, Cadmium, Cobalt, Nickel, and Manganese.**—Having precipitated the cadmium from the acidulated solution by sulphuretted hydrogen, and reconverted the iron into sesquioxide by boiling the liquid with a small quantity of nitric acid, it is to be largely diluted with water, and sodic carbonate added gradually until a permanent precipitate is formed, although the liquid still remains faintly acid to test paper. The solution must be boiled, and the liquid filtered from the bulky precipitate of the basic ferric salt: the clear solution must then be slightly supersaturated with sodic carbonate, and afterwards feebly acidulated with acetic acid: on again boiling the liquid, the last trace of iron is thrown down in the form of basic acetate, whilst the other metals are retained in the solution: the precipitated ferric salt must be redissolved in hydrochloric acid, and the iron thrown down as sesquioxide by the addition of ammonia.

Sometimes ammonia in excess is made use of to separate iron from these metals, which all form soluble compounds with ammonia, and which it is supposed will retain them in solution; but this method should never be resorted to in analysis, because the precipitated ferric oxide always carries down with it a large quantity of the other oxides.

(882) **Separation of Iron from Uranium.**—The iron having been converted into sesquioxide is precipitated by a large excess of ammonic sesquicarbonate, which retains most of the uranium. This process, however, although usually adopted, is imperfect; for if the quantity of iron be at all large, a considerable proportion of uranium is precipitated along with it.

(883) **Estimation of Ferrous Salt in a mixture of Ferric and Ferrous Salts.**—It often happens that the chemist has to ascertain the relative proportions of ferrous and ferric oxide which a compound contains. If the compound of iron for examination be soluble in hydrochloric acid, the following process by Penny

will be found both easy of execution and accurate in its results. It is based upon the power which a solution of the potassic dichromate (bichromate) in excess of hydrochloric acid possesses of converting ferrous chloride into ferric chloride, whilst the chromic acid is reduced to the state of chromic chloride; $K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7OH_2$. In order to carry this process into effect, 4·44 grams of pure potassic dichromate are introduced into an alkalimeter burette of 100 cub. centim. (610), which is to be filled up to 0° with tepid water; the mixture is to be agitated until the salt is dissolved. Each division of the instrument contains sufficient of the dichromate to convert 50 mgrms. of metallic iron, in the form of ferrous chloride, into ferric chloride. The ore for experiment having been reduced to an extremely fine powder, 10 grams of it are boiled in a flask for ten or fifteen minutes with about 80 cub. centim. of hydrochloric acid of density 1·100: about 200 cub. centim. of boiling distilled water are added, and the mixture immediately transferred to an evaporating basin, taking care to rinse out the flask thoroughly. A white plate is then spotted over with a few drops of a weak solution of potassic ferricyanide, and the dichromate is cautiously added from the alkalimeter to the solution of iron (which is kept in continual agitation), until it assumes a dark-greenish shade; as soon as this begins to appear, it must be tested after each addition of the dichromate, by taking out a drop of the solution on a glass rod, and adding it to one of the drops of the ferricyanide. When the last drop no longer occasions a blue precipitate, the operation is ended, and the number of divisions of the liquid which has been added, when divided by two, indicates the amount of metallic iron which exists in the form of a ferrous compound in 100 parts of the ore. The total quantity of iron present in the solution may be ascertained by making a second experiment on a fresh portion of the ore, and reducing the metal, whilst still in the flask with the hydrochloric acid, to the state of the ferrous salt: this is readily effected, either by passing a current of sulphuretted hydrogen and then expelling the excess of that gas by ebullition; or by boiling the concentrated solution with metallic zinc, or by nearly neutralizing the liquid with sodic carbonate, and adding a solution of sodic sulphite until a drop of the liquid ceases to give a red colour when mixed with a drop of a solution of potassic sulphocyanide,* placed upon a white plate: the liquid is

* The reducing effect of sodic sulphite on the ferric chloride may be explained

then boiled, to expel the excess of sulphurous acid. When the iron has thus been reduced to the state of ferrous salt, the whole quantity of the metal present may be ascertained by means of the solution of potassic dichromate, as before; the difference between the two results will give the per-centage of metallic iron present in the form of ferric salt.

Another excellent process for determining the amount of a ferrous salt present was contrived by Margueritte (*Ann. Chim. Phys.*, 1846, [3], xviii. 244). It consists in ascertaining the quantity of a measured solution of potassic permanganate of known strength, which the cold acidulated and largely diluted solution of iron in hydrochloric acid, can deoxidize and deprive of colour, according to the reaction expressed in the following equation; $K_2Mn_2O_8 + 10Fe''Cl_2 + 16HCl = 2MnCl_2 + 2KCl + 5Fe''_2Cl_6 + 8OH_2$. The strength of the solution of permanganate is ascertained by dissolving 0·5 gram of clean iron wire in boiling hydrochloric acid, diluting the solution largely, and ascertaining the number of divisions of permanganate measured from a burette, which it is capable of decolorizing.

The total quantity of iron present in an ore or other compound may be ascertained by a second experiment upon a fresh portion of the ore, reducing the iron to the state of a ferrous salt by means of zinc, or otherwise, as described when treating of Penny's process.

(884) **Analysis of Cast Iron, Steel, and Bar Iron.**—For this purpose the metal must be reduced to a fine state of subdivision by means of a new file, previously freed from oil by the action of a solution of potash; the fine particles detached are to be sifted through a lawn sieve. Some kinds of cast iron are too hard to admit of being filed; they must be crushed in a small mortar made of hard steel.

1. The proportion of *carbon* is ascertained by mixing from 3 to 6 grams of finely-divided iron with about 10 times its weight of plumbic chromate or of cupric oxide; then placing it in an apparatus similar to that shown in fig. 306, p. 132, and burning the iron in a very gentle current of oxygen: the carbonic anhydride which is formed is collected in a solution of potash placed in Liebig's bulbs. The tube which contains the iron is gradually heated with charcoal, commencing at the extremity nearest the potash bulbs, and the fire is slowly advanced towards the other end, until, when the operation is completed, the whole length of the tube is red hot. From the quantity of carbonic anhydride thus obtained, the proportion of carbon in the iron may be calculated. A less rapid but much more accurate plan consists in digesting the iron in filings or in fragments with an excess of normal cupric chloride ($CuCl_2$) dissolved in water; the iron is slowly dissolved, and copper precipitated in its place, whilst the carbon

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by the following equation, from which it will be seen that the sodic sulphite is converted into sulphate during the operation; $Fe'''_2Cl_6 + OH_2 + Na_2SO_3 = 2Fe''Cl_2 + 2HCl + Na_2SO_4$.

is left in a finely-divided condition. The precipitate must be collected on a filter, dried, and transferred to a tube in which it is burned in the manner above described. It has been already explained that cast iron contains carbon partly in chemical combination, partly in a state of mechanical mixture, and it is important to determine the relative proportions of the carbon which exist in these different conditions. This may be effected by dissolving the iron in hydrochloric acid. In this operation all the carbon which was chemically combined with the iron is separated in the form either of a gaseous compound of carbon and hydrogen, or as a liquid hydrocarbon; whilst the scales of graphite mechanically diffused through the metal are not acted upon by the acid, and are left in a solid form mixed with silica. In order to ascertain the proportion of graphite in this residue, it is collected on a small weighed filter, and washed with ether, to remove any adhering liquid hydrocarbon; the filter and its contents are dried at 100° (212° F.), and weighed in a covered crucible. The residue is then burned, and the silica which remains is deducted from the weight of the precipitate collected on the filter.

2. *Nitrogen.*—Two methods were employed by Boussingault for ascertaining the amount of nitrogen: the first consisted in oxidizing a known weight of iron by heating it to redness in a current of steam, condensing the water after it had passed over the iron, and determining the amount of ammonia that it contained, by a method previously contrived by him for ascertaining its amount in rain-water: the second consisted in converting a given weight of iron into sulphide, by heating it with cinnabar, and measuring the amount of nitrogen in the gaseous state by a method exactly analogous to that invented by Dumas for determining the amount of nitrogen in an organic body. For details, the reader is referred to the original papers in the *Compt. Rend.* (lii. pp. 1008 and 1250).

3. The quantity of *silicon* contained in the iron is ascertained by dissolving the metal in hydrochloric acid and evaporating the solution to dryness, moistening with concentrated hydrochloric acid, then dissolving all the soluble matter in water, and collecting the silica on a filter: from this residue, after the graphite is burned off, the quantity of silicon can be estimated, 100 parts of silica representing 46·66 of silicon. The silicon may also be estimated by oxidizing the iron or steel by ignition in a muffle, and heating the resulting oxide in a current of dry hydrochloric acid: the iron is volatilized as chloride, and the silicon is left as pure silica.

4. *Sulphur*, *Phosphorus*, and *Arsenicum.*—The most accurate mode of estimating these substances consists in deflagrating about 3 grams of finely-powdered iron with about six times its weight of a mixture of 5 parts of pure nitre, and 1 part of potassic carbonate, in a crucible of silver, or, still better, of gold.* The phosphorus, sulphur, and arsenicum are thus converted into phosphoric, sulphuric, and arsenic anhydrides, which form salts by their action upon the potassic carbonate; when the fused mass is digested in water they are dissolved out from the insoluble ferric oxide. The filtered solution is supersaturated with hydrochloric acid, and the sulphuric acid is thrown down by means of baric chloride; after collecting the baric sulphate, the excess of barium is removed from the filtrate by adding sulphuric acid, and the arsenic is thrown down as orpiment by a current of sulphuretted hydrogen. The liquid, filtered from the orpiment, is now neutralized by ammonia, and on the addition of a few drops of a solution of magnesic sulphate, the phosphoric acid is gradually precipitated as the crystalline ammonic magnesic phosphate.

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* Any traces of vanadium or of chromium would also be oxidized, and on digesting the mass in water would be dissolved out in the alkaline liquid.

The ferric oxide is dissolved in hydrochloric acid, and a current of sulphuretted hydrogen is passed through the liquid, by which copper is separated as sulphide; the filtrate is boiled with nitric acid, and the iron separated from manganese, cobalt, or nickel, by means of sodic carbonate in the manner already described (881).

The sulphur may also be estimated by treating the iron with an acid, and absorbing the liberated sulphuretted hydrogen by pure soda, and determining its amount by means of a standard solution of iodine.

§ V. CHROMIUM: Cr=52·5.

(885) **CHROMIUM:** *Density, 6·81; Dyad, in Chromous Salts, as* $CrCl_2$; *Pseudo-triad, in Chromic Salts, as* Cr_2Cl_6 $\left[\begin{matrix}CrCl_3\\CrCl_3\end{matrix}\right]$, *occasionally Hexad, as in* CrF_6.—This is a metal which is but sparingly distributed over the earth. Its most important ore is chrome ironstone, a compound of ferrous oxide with chromic oxide, $FeO.Cr_2O_3$; it is generally found massive, but has now and then been met with crystallized in regular octahedra like the magnetic oxide of iron, to which it corresponds in composition: it is principally supplied from North America and from Sweden. Occasionally the metal occurs in a higher state of oxidation, in combination with lead, as plumbic chromate, $PbCrO_4$. Indeed it was in this beautiful mineral that Vauquelin, in the year 1797, first discovered the existence of chromium.

To obtain the metal, finely-powdered chromic oxide is intimately mixed with charcoal, and made up into a paste with oil; it is then placed in a crucible lined with charcoal, the cover of the crucible is luted on, and it is exposed for two hours to the heat of a good wind furnace: an agglomerated mass of metallic appearance is thus obtained. It is not pure chromium, but consists of a combination of carbon with the metal. Chromium obtained by this method is very difficult of fusion: it generally forms a porous mass composed of brilliant grains, which are hard enough to scratch glass. In this state it has a density of about 5·9, which is no doubt lower than it would be after complete fusion. Deville found, on reducing chromium from pure sesquioxide by means of charcoal from sugar, in quantity sufficient for complete reduction, that the mass underwent partial fusion, but could not be melted into a complete button even at a temperature sufficient to fuse and volatilize platinum. If ignited with the hydrated alkalies, alkaline carbonates, or nitrates, chromium is rapidly converted into a chromate by action on the alkaline base. It may, however, be heated to redness in the open air without becoming oxidized, and is not acted on by any acid except hydrofluoric acid.

Fremy passes the vapour of sodium over chromic chloride, which is placed in a porcelain tray, and heated to redness in a porcelain tube: the chromium is obtained in brilliant crystals, which, according to Bolley, are quadratic octahedrons; they are insoluble in aqua regia. Wöhler reduces chromium from the violet chloride by fusing it with twice its weight of zinc under a flux of the mixed potassic and sodic chlorides: nitric acid is employed to dissolve the zinc, and the chromium is left as a grey, brilliant, crystalline powder

of density 6·81. Zettnow (*Pog. Ann.*, 1871, cxliii. 477) prefers to fuse with zinc, the double chloride of potassium and chromium obtained by reducing potassic dichromate with hydrochloric acid and alcohol, adding the proper quantity of potassic chloride to the solution, and evaporating to dryness. If chromic chloride be mixed with potassium, and heated in a covered crucible, another modification of chromium may be obtained; after washing the residue with water, the metal remains in the form of a dark-grey powder which assumes a metallic lustre under the burnisher. This pulverulent chromium, if heated in the air, takes fire below redness, and burns brilliantly: it is oxidized with great violence by nitric acid, sometimes becoming incandescent during the action, and it is dissolved by hydrochloric acid and dilute sulphuric acid with evolution of hydrogen.

An amalgam of chromium is obtained on treating a solution of chromic chloride with sodium amalgam, which, when heated in a current of hydrogen, leaves metallic chromium in the form of a pulverulent sponge (Vincent).

Metallic chromium has not been applied in the arts, but its sesquioxide and many of the chromates are highly valued as colouring materials, both in painting on porcelain, and in calico-printing.

(886) **CHLORIDES OF CHROMIUM.**—Chromium forms two chlorides, chromous chloride, $CrCl_2$, and chromic chloride, Cr_2Cl_6: the latter is the more important. It also forms an oxychloride, $CrCl_2O_2$, frequently termed chlorochromic acid (895).

Chromous Chloride (Péligot's *protochloride*, $CrCl_2 = 123{\cdot}5$) is obtained by heating chromic chloride to redness in a current of dry hydrogen (carefully freed from every trace of oxygen): it is a white substance which is readily dissolved by water, forming a blue solution which absorbs oxygen rapidly, and becomes green: like ferrous chloride, it rapidly absorbs nitric oxide forming a dark brown solution.

Chromic Chloride, formerly *Sesquichloride of chromium*, $Cr_2Cl_6 = 318$.—When a current of dry chlorine is passed over an intimate mixture of finely-divided chromic oxide and charcoal, heated to redness in a glass tube, beautiful pale violet-coloured scales of anhydrous chromic chloride sublime. When rubbed upon the skin they have a soapy feel: they are quite insoluble in cold water, but by boiling them with water for some time, a green solution is gradually formed. Sulphuric and hydrochloric acids, and even aqua regia, do not dissolve them. It is, however, very remarkable that the change from this insoluble to the soluble green variety is effected in a few moments with development of heat, if a minute quantity of chromous chloride is added to the insoluble chloride suspended in water. When the green hydrated chromic oxide is dissolved in hydrochloric acid, a similar green solution is formed; by spontaneous evaporation the liquid furnishes green crystals, the composition of which, according to Péligot, may be represented by the formula, $Cr_2O_2Cl_2{\cdot}4HCl{\cdot}10OH_2$; for it is singular that only two-thirds of

the chlorine which this solution contains is precipitated when it is mixed with argentic nitrate (*Ann. Chim. Phys.*, 1844, [3], xii. 536; 1845, xiv. 239; and 1846, xvi. 294). A soluble violet chloride of the metal which contains the same proportion of chlorine may be formed by precipitating the violet-coloured chromic sulphate by an equivalent quantity of baric chloride: argentic nitrate precipitates the whole of the chlorine from this solution.

(887) **CHROMIC HEXAFLUORIDE,** or *Fluoride of chromium*, $CrF_6 = 166{\cdot}5$, is obtained by distilling 4 parts of plumbic chromate, 3 of powdered fluor-spar, and 8 of strong sulphuric acid, in a platinum retort; sulphates of lead and calcium are formed, and the hexafluoride distils as a deep red vapour, which by a low temperature is reduced to a blood-red liquid; $PbCrO_4 + 3CaF_2 + 4H_2SO_4 = PbSO_4 + 3CaSO_4 + 4OH_2 + CrF_6$. Any other chromate may be substituted for plumbic chromate in this operation.

Chromic hexafluoride is decomposed by moisture, and consequently forms deep red fumes of chromic anhydride the moment that it comes in contact with the air: by conducting the vapour into a moistened platinum crucible, the vessel becomes speedily filled with voluminous crystals of chromic anhydride; hydrofluoric acid is formed at the same time, and may be expelled from the chromic anhydride by a gentle heat. The action of water upon the hexafluoride may be thus represented: $CrF_6 + 3OH_2 = CrO_3 + 6HF$.

(888) **OXIDES OF CHROMIUM.**—Chromium forms five well-marked oxides: a protoxide, CrO, and a sesquioxide, Cr_2O_3, both capable of forming salts with acids; an intermediate oxide, $CrO.Cr_2O_3$, corresponding to the magnetic oxide of iron; a stable anhydride, CrO_3, which by its action on bases forms salts corresponding to the manganates and ferrates; and a dioxide or *chromic chromate*, Cr_3O_6, or $Cr_2O_3.CrO_3$ (p. 671). It also appears to be probable that a perchromic acid, $H_2Cr_2O_8$, exists; at least, a blue liquid, which is soluble in ether, is obtained on pouring hydric peroxide into a solution of chromic acid: none of its compounds are known, however.

(889) **CHROMOUS OXIDE,** or *Protoxide of chromium;* $CrO = 68{\cdot}5$. —This oxide is known only in the hydrated condition. It is obtained as a dark-brown precipitate on adding potassic hydrate to a solution of chromous chloride; it absorbs oxygen with great avidity, and even decomposes water with evolution of hydrogen, being converted into the intermediate hydrated oxide, $CrO.Cr_2O_3.OH_2$, which is of the colour of Spanish snuff (Péligot, *Ann. Chim. Phys.*, 1844, [3], xii. 541).

Chromous oxide forms a double sulphate with potassic sulphate, $Cr''K_2SO_4.6OH_2$, corresponding to the ferrous potassic sulphate both in form and composition. The crystals are of a fine blue colour.

(890) **CHROMIC OXIDE,** or *Sesquioxide of chromium*, $Cr_2O_3 = 153$; *Density, cryst.* 5·21; *Comp. in* 100 *parts*, Cr, 68·63; O, 31·37.—This oxide is obtained as a greyish-green hydrate, by

boiling with alcohol a solution of potassic dichromate (bichromate) acidulated with sulphuric acid. The alcohol deprives the chromic acid of half its oxygen, and the liquid becomes green from the formation of chromic sulphate. A current of sulphurous anhydride may be employed instead of alcohol in the reduction of chromic acid. On the addition of ammonia, a bulky, gelatinous bluish-green precipitate of the hydrated sesquioxide is produced, which retains alkali with great obstinacy even when boiled with water. In this form it is freely soluble in acids, and forms salts, the solutions of which are of a green colour; they do not crystallize.

Chromic oxide gives rise also to another set of soluble salts, which are of a violet colour and crystallize readily. When these violet-coloured salts are precipitated by ammonia, they give a bluish-green hydrated sesquioxide, which if redissolved in an acid without the application of heat, reproduces the violet-coloured salts. This precipitated oxide becomes green by the action of concentrated saline solutions upon it. If a solution of one of the violet salts be heated to the boiling-point, or a little short of it, the salt at once becomes green.

This change of colour from violet to green has been long known, and was accounted for by Berzelius upon the admission of two distinct hydrates of chromic oxide, one green, the other violet. But Siewert appears to have distinctly proved that one form only of the sesquioxide, the blue hydrate, exists. The green precipitate in every instance is a compound of the pure oxide with potash or soda. It is true that the violet solutions of the pure salts become green by boiling, but this Siewert has traced to the conversion of the normal salt into two soluble salts, each green, and capable of co-existing in the liquid. One of these salts contains excess of acid, the other excess of base (*Ann. Chem. Pharm.*, 1863, cxxvi. 86). Solutions of the green salts at once become blue or violet, if acidulated with nitric acid. The investigation of these compounds is beset with unusual difficulties.

The hydrated sesquioxide from the violet salts is the *metachromic* oxide of Fremy ($Cr_2O_3.9OH_2$, when dried *in vacuo*), and is soluble in excess of ammonia in the presence of acetic acid: but according to Siewert, who has since examined this precipitate with great care, it is not a pure sesquioxide, but a compound of the hydrated sesquioxide with ammonia and one of the salts of ammonium. It is soluble in excess of ammonia and acetic acid, owing to the strong tendency of chromic oxide and ammonia to produce, in the presence of acetic acid, double salts, which are not susceptible of decomposition by ammonia. If the original precipitate be thoroughly washed until all the soluble salts are removed from it, and then air dried, it is no longer soluble in acetic acid, or in dilute mineral acids.

The only way to insure the production of a pure hydrated chromic oxide, according to Siewert, consists in precipitating a soluble chromic salt by the addition of ammonia, and boiling it with excess of the alkali. A light-blue precipitate is thus

obtained, which, when well washed and dried in air over oil of vitriol, consists of $Cr_2O_3.7OH_2$. If dried *in vacuo*, it retains only $4OH_2$, and if dried in a current of hydrogen at 200° (392° F.), it retains OH_2; it then forms a blue powder with a greenish lustre, and is insoluble in boiling dilute hydrochloric acid. Potassic and sodic hydrates precipitate the hydrated sesquioxide, and redissolve it if added in excess, forming a green solution, from which, on boiling, the whole of the chromic oxide is separated as a green hydrate, which retains a portion of the alkali. Indeed, potash and soda have so strong a tendency to combine with chromic oxide that if either of these alkalies be used to precipitate the oxide from its salts, or if salts of potash or soda be present when ammonia is employed as the precipitant, the green precipitate always contains one of the fixed alkalies. When the hydrated sesquioxide is heated, it parts with its water below redness, and if heated a little beyond this point, it suddenly becomes incandescent, and shrinks considerably in bulk, after which it is no longer attacked by acids.

Besides the soluble variety of the salts of chromium, an anhydrous, insoluble series is known, corresponding, it would seem, to the dense and comparatively inert modification of the metal itself.

Anhydrous chromic oxide is obtained in beautiful dark green rhombohedral crystals when the vapour of chromic oxydichloride is passed through a porcelain tube heated to redness; these crystals, which are isomorphous with corundum, are hard enough to cut glass. During their formation, oxygen and chlorine escape, as represented in the following equation, $4CrCl_2O_2 = 2Cr_2O_3 + 4Cl_2 + O_2$. When ammonic dichromate is heated, an energetic action takes place, and a bulky mass of chromic oxide is left, somewhat resembling green tea in appearance.

Anhydrous green chromic oxide is not decomposed by heat, and hence is used as a green colour in enamel painting. It is usually prepared for this purpose by decomposing basic mercurous chromate by a red heat: half the oxygen of the anhydride is expelled along with the mercurous oxide. Ammonic chromate may be employed instead of mercurous subchromate with equally good results. Another method consists in igniting strongly, in a covered crucible, an intimate mixture of 4 parts of powdered potassic chromate and 1 part of starch; the potassic carbonate resulting from the decomposition is washed out, and the chromic oxide which remains, after undergoing a second calcination, yields a beautiful clear green colour. There are also various other modes of obtaining it. Chromic oxide is the colouring ingredient

in greenstone, in the emerald, in pyrope, and in several other minerals. The *pink colour* used on earthenware is prepared by heating to redness a mixture of 30 parts of stannic oxide, 10 of chalk, and 1 of potassic chromate; the product is then finely powdered, and washed with dilute hydrochloric acid; a beautiful rose-tint is thus obtained.

A beautiful green pigment known as *vert de Guignet* is manufactured on a large scale by calcining potassic dichromate with 3 times its weight of crystallized boric acid: oxygen and water are expelled, and on washing the residue with water a (?) basic chromic borate is left, whilst boric acid and potassic borate are dissolved out.

(891) **CHROME IRONSTONE**, $FeO.Cr_2O_3$; *Density*, 4·5, is the principal ore of chromium: it corresponds in composition with brown oxide of chromium, and with magnetic oxide of iron; part of the iron is, however, generally displaced by the isomorphous metal magnesium, and part of the chromium by aluminium. Like magnetic iron ore, chrome ironstone often crystallizes in octahedra, which have about the same hardness as felspar. Chrome ironstone is scarcely attacked by any of the acids. It is infusible in the furnace, and when heated absorbs oxygen from the air; this oxidation takes place rapidly when it is powdered and mixed with a carbonate of one of the metals of the alkalies or alkaline earths, a chromate of the base being formed. 100 parts of this ore, if pure, should contain 46·667 of chromium, and correspond to 89·333 of chromic anhydride.

(892) **Ammoniacal Compounds of Chromium.**—Fremy believes in the existence of a series of ammoniated compounds of chromium presenting some analogy with those of cobalt. If a saturated solution of sal ammoniac in ammonia be digested with the hydrated sesquioxide precipitated by ammonia from one of the violet chromium salts, the oxide is dissolved, and a deep rose-coloured solution is formed. If this be exposed to the air, a violet-coloured amorphous powder is deposited, which is soluble in dilute hydrochloric acid. From this solution bright red rhombic prisms may be obtained, which, according to Cleve, are *tetramine chromic chloride*, and have the composition, $Cr_2Cl_6.8NH_3.2OH_2$. Other salts corresponding to this chloride have been prepared. When their solutions are boiled, ammonia is expelled and hydrated chromic oxide is precipitated.

(893) **CHROMIC ANHYDRIDE**, formerly **Chromic Acid**, $CrO_3 = 100·5$; *Density*, 2·676.—There are several modes of obtaining this compound. 1.—The simplest consists in mixing 4 measures of a cold saturated solution of potassic dichromate with 5 of oil of vitriol: as the liquid cools, the chromic anhydride separates in beautiful crimson needles; for although very soluble in water, this compound has the peculiarity of being nearly insoluble in sulphuric acid of density 1·55, but is freely dissolved

by it either in a more concentrated or in a more dilute condition. The crystals are allowed to dry upon a porous tile, under a bell-glass. A good deal of sulphuric acid, however, still adheres to them; in order to remove it, the crystals should be dissolved in water, and a solution of baric dihydric chromate, $BaH_2 2CrO_4$, added in quantity just sufficient to throw down the whole of the sulphuric acid as baric sulphate: the solution may be recrystallized by evaporation *in vacuo*. (See also Zettnow, *Pog. Ann.*, 1871, cxliii. 468, and *Jour. Chem. Soc.*, 1872, xxv. 45.) 2—Chromic anhydride may also be obtained from the chromic hexafluoride, CrF_6, by decomposing this compound with water (887). 3.—It can likewise be prepared from baric chromate, 100 parts of which are mixed with 100 of water, and 140 of nitric acid (density 1·357) added. It is then heated until it becomes red, 200 more of water are added, and the whole boiled for 10 minutes. On cooling, most of the baric nitrate crystallizes out, and almost the whole of the remainder may be separated by evaporating the liquid until its volume equals that of the acid originally taken. The excess of nitric acid is removed by evaporating once or twice with water (Duvillier, *Compt. Rend.*, 1872, lxxv. 711).

Chromic anhydride is easily freed from water by drying it at a gentle heat. While hot, it is black, but it becomes dark red on cooling: at about 200° (392° F.) it fuses, and if heated more strongly becomes vividly incandescent and is converted into the sesquioxide with disengagement of oxygen. The anhydride deliquesces when exposed to the air. Its solution has a sour, metallic taste, and possesses considerable oxidizing power, from the facility with which it is reduced to chromic oxide. When heated with hydrochloric acid, chlorine is evolved and chromic chloride is formed; $2CrO_3 + 12HCl = Cr_2Cl_6 + 6OH_2 + 3Cl_2$. The anhydride forms more than one crystalline compound with sulphuric acid; these compounds are decomposed by water. Chromic anhydride is the colouring matter of the ruby.

(894) **Chromates.**—Chromic acid is dibasic; it forms 3 classes of salts—basic, normal, and acid. The chromates of the alkali-metals are soluble in water; the normal salts, which are of a yellow colour, have the general formula, M'_2CrO_4; the acid salts are of a bright orange: the most important of these salts are the potassic chromate, and the anhydro-chromate or dichromate, from which the other chromates are generally obtained. Chromic acid, like iodic acid, is remarkable for the anhydro-salts which it forms with potash; it yields four salts with this base, known respectively as: 1, the chromate, $K_2O.CrO_3$; 2, the dichromate or bichromate,

$K_2O.2CrO_3$; 3, the trichromate, $K_2O.3CrO_3$; and 4, the tetrachromate of potash, $K_2O.4CrO_3$.*

Potassic dichromate, pyrochromate or *anhydro-chromate,* or *Bichromate of potash,* $K_2O.2CrO_3$, or $K_2Cr_2O_7 = 295{\cdot}2$; *Density,* 2·624; *Comp. in* 100 *parts,* K_2O, 31·91; CrO_3, 68·09.—This salt crystallizes in large red, transparent, anhydrous four-sided tables, and is analogous in composition to potassic pyrosulphate, $K_2S_2O_7$; it would thus be a normal salt, which is in accordance with the fact pointed out by Mohr that potassic dichromate does not decompose potassic iodide. It fuses below redness, to a deep red liquid which solidifies to a mass of crystals that split up as they cool, probably owing to a change of form. By heating the dichromate to bright redness, normal potassic chromate and green chromic oxide are formed, whilst oxygen escapes. It requires about 10 times its weight of water at 15° (59° F.) for solution.

In order to procure potassic anhydro-chromate, chrome ironstone is heated to redness and quenched in cold water, by which means it is rendered friable, and is then reduced to an extremely fine powder, and heated to bright redness in a current of air in a reverberatory furnace with a mixture of chalk and potassic carbonate, the mixture being constantly stirred to hasten the oxidation. When this is complete, the product is digested in water, potassic carbonate being added, if necessary, to decompose any calcic chromate which may have been formed; the yellow solution is then drawn off from the insoluble matter, and supersaturated with nitric acid; a portion of silica is thus precipitated, and after this has been separated, the liquid, on evaporation, yields crystals of potassic dichromate, which are purified by recrystallization. The addition of chalk in the furnace favours the oxidation by preserving the mass in a porous condition: if potash alone were used, it would fuse, and the chrome ore would fall to the bottom.

According to Schweitzer, several double salts may be formed by digesting potassic dichromate with an equivalent of some base, such as lime or magnesia. The magnesic potassic chromate

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* [1. $CrO_2(OK)_2$ 2. $CrO_2(OK)$, O, $CrO_2(OK)$ 3. $CrO_2(OK)$, O, CrO_2, O, $CrO_2(OK)$ 4. $CrO_2(OK)$, O, CrO_2, O, CrO_2, O, $CrO_2(OK)$].

crystallizes in oblique rhombic prisms, $K_2Mg2CrO_4.2OH_2$, and a similar calcic potassic chromate may be obtained; but there is no analogy between these double chromates and the magnesian double sulphates.

If a solution of potassic carbonate be added to the dichromate, until it becomes of a pale yellow colour, carbonic anhydride is expelled, and the *normal potassic chromate* ($K_2CrO_4 = 194{\cdot}7$; *density*, 2·682), is formed. This salt, which is of an intense yellow colour, is soluble in about twice its weight of cold water, and still more freely in boiling water, a very small quantity of the salt sufficing to impart a yellow tinge to a considerable volume of water. By the evaporation of its solution, potassic chromate may be obtained with some difficulty in transparent, yellow, anhydrous prisms, which are isomorphous with those of potassic sulphate: at a red heat it fuses without undergoing decomposition. A *trichromate*, $K_2O.3CrO_3$, also anhydrous, was obtained by Mitscherlich in deep red crystals, by adding an excess of nitric acid to a solution of the dichromate, and allowing it to evaporate. Siewert has obtained a *tetrachromate*, $K_2O.4CrO_3$, in thin, red, brilliant prismatic plates, by evaporating a solution of the trichromate in nitric acid at a gentle heat. According to Darmstädter (*Deut. chem. Ges. Ber.*, 1871, iv. 167), when potassic dichromate is dissolved in 2 parts hot concentrated nitric acid, it deposits, on cooling, magnificent crimson plates having the formula, $KNO_3.2CrO_3$.

Sodic chromate, $Na_2CrO_4.10OH_2 = 162{\cdot}5 + 180$, may be obtained by a process similar to that employed in preparing potassic chromate: it forms efflorescent crystals: a *hydric sodic chromate*, $2(NaHCrO_4).OH_2$, may likewise be obtained in ruby red crystals.

Ammonic dichromate, $(NH_4)_2O.2CrO_3$, is easily obtained in orange-red crystals by dividing a solution of chromic acid into two parts, neutralizing one with ammonia, adding the other, and evaporating: by the action of heat it is decomposed, leaving pure chromic oxide (890).

Calcic chromate is soluble, as is also the *acid-chromate*, which is formed in many chrome works as a preliminary stage in the manufacture of the chromates. Jacquelain decomposes chrome ore by roasting it in fine powder intimately mixed with chalk, grinds the roasted mass with water, and adds sulphuric acid until the liquid has an acid reaction, in which case dihydric calcic chromate is formed, and remains in solution. Calcic chromate has been used by Shanks for the preparation of chlorine by the action of hydrochloric acid upon it; $2CaCrO_4 + 16HCl = 2CaCl_2 + Cr_2Cl_6 + 8OH_2 + 3Cl_2$; to the solution thus produced lime is added, which precipitates chromic hydrate, calcic chloride remaining in solution. The chromic hydrate is then roasted at a low red heat with lime, when calcic chromate is reproduced, $4CaO + 2Cr_2H_6O_6 + 3O_2 = 4CaCrO_4 + 6OH_2$, which may be employed for another operation. It will be seen that only six-sixteenths of the chlorine in the hydrochloric acid is evolved in the free state. *Baric chromate* ($BaCrO_4 = 253{\cdot}5$; density 3·9Q) is a canary-yellow insoluble powder: it dissolves

in a boiling solution of chromic acid, and on cooling *baric dichromate*, $BaCr_2O_7$, is deposited as a yellowish-red powder. *Strontic chromate* is yellow and but slightly soluble.

Chromic chromate, $Cr_2O_3.CrO_3$, or *chromic dioxide*, may be obtained by heating equal parts of potassic dichromate and oxalic acid with strong nitric acid, evaporating and fusing; or more conveniently by passing nitric oxide into a dilute solution of potassic dichromate. It forms a dark brown or black powder which is very hygroscopic.

Plumbic chromate, or *Chromate of lead* ($PbCrO_4=323{\cdot}5$; *density*, 5·653), forms the pigment called 'chrome yellow.' It is obtained by precipitating a somewhat dilute solution of plumbic acetate by one of potassic chromate or dichromate. Plumbic chromate is insoluble in water and in acids, but like all the insoluble lead salts, it is dissolved by a large excess of potassic or sodic hydrate. Concentrated nitric acid decomposes it, forming plumbic nitrate and chromic anhydride. When heated to 200° (392° F.) or 250° (482° F.), its colour becomes reddish-brown; at a higher temperature it fuses, and when heated still more strongly, it gives off about 4 per cent. of oxygen, chromic oxide and basic plumbic chromate being formed; $8PbCrO_4=4(PbCrO_4.PbO)+2Cr_2O_3+3O_2$. Fused plumbic chromate when reduced to powder is sometimes advantageously substituted for cupric oxide in the combustion and analysis of organic substances very rich in carbon. A *dibasic plumbic chromate* ($2PbO\ CrO_3$; *density*, 6·266), of a splendid scarlet colour, may be obtained by boiling a solution of the yellow plumbic chromate with half an equivalent of lime, or by adding to a solution of plumbic nitrate a solution of potassic chromate, with which an additional equivalent of potassic hydrate has been previously mixed. It may be obtained of a still more brilliant colour by fusing 1 part of the normal plumbic chromate with 5 parts of nitre; potassic chromate and dibasic chromate of lead are formed; the potassium salt may be removed by washing. The salt is used to impart a permanent orange to calico: it is easily formed upon the fabric by first dyeing it yellow with normal chromate of lead, and then boiling it with lime-water, by which half the chromic acid is abstracted, and the dibasic chromate is left attached to the fibre.

Basic mercurous chromate, $3Hg_2CrO_4.Hg_2O$, falls as an orange-coloured insoluble precipitate on adding basic mercurous nitrate to a soluble chromate. *Argentic chromate* (Ag_2CrO_4; *density* 5·77), is of a dark red colour, the tint of which is deeper if the solutions be mixed whilst hot: it is crystalline, and sparingly soluble.

An *argentic dichromate*, $Ag_2O.2CrO_3$, is obtained in beautiful crimson tables by heating metallic silver with potassic dichromate and sulphuric acid, chrome-alum being formed during the process:

$$3Ag_2+4K_2Cr_2O_7+7H_2SO_4=3Ag_2Cr_2O_7+K_2Cr_24SO_4+3K_2SO_4+7OH_2.$$

Dichromate of chloride of potassium, $KCl.CrO_3$? or $K_2CrO_4.CrO_2Cl_2$ [$CrO_2Cl(OK)$]; *Density*, 2·466.—This remarkable compound, sometimes called *potassic chlorochromate*, may be obtained crystallized in orange-coloured needles, by dissolving 3 parts of potassic dichromate and 4 of hydrochloric acid in a little water at a gentle heat, and allowing it to cool: a large quantity of water decomposes the salt. An ethereal solution of ammonia converts it into *potassic amidochromate*, KNH_2CrO_3, which may be crystallized from boiling water.

Potassic bromochromate and *potassic iodochromate* have also been obtained by treating potassic dichromate with concentrated hydrobromic and hydriodic acids.

(895) **Chromic Oxydichloride**, or **Chlorochromic Acid**; $CrCl_2O_2 = 155·5$; *Theoretic density of vapour*, 5·38; *Observed*, 5·52; *of liquid*, 1·92; *Mol. vol.* [ ]; *Boiling-pt.* 118° (244°·4 F.).—This is a dense red liquid, which emits copious red fumes of a suffocating odour; it is immediately decomposed by water into chromic and hydrochloric acids. When dropped into a strong solution of ammonia or into alcohol, it bursts into flame from the intensity of the reaction. When heated in a sealed tube at 180° to 190° (356° to 374° F.) for three or four hours, it is almost entirely resolved into *chromium chromatochloride*, $Cr_3Cl_2O_6$ or $Cr''Cl_2.2CrO_3\left[\begin{matrix}CrO_2Cl\\CrO_2\\CrO_2Cl\end{matrix}\right]$ and chlorine. The product may be freed from chromic oxychloride by heating it at 120° (248° F.) in a current of carbonic anhydride. It is a dark coloured powder which rapidly deliquesces on exposure to the air. According to MacIvor (*Chem. News*, 1873, xxviii. 138), it can also be obtained by heating chromic dichloride with iodine; $3CrCl_2O_2 + 2I_2 = Cr_3Cl_2O_6 + 4ICl$. It likewise appears to be produced, together with chlorochromic acid, by the action of fuming sulphuric acid on potassic chlorochromate.

Chlorochromic acid is analogous to the chloromolybdic, chlorotungstic, and chlorosulphuric acids in composition, and in the products which it yields when decomposed. In order to prepare it, 10 parts of common salt are fused with 17 of potassic chromate; the melted mass, when cold, is broken into fragments, and gently heated in a retort with 30 parts of oil of vitriol: the chlorochromic acid distils over readily.

(896) **CHROMIC SESQUISULPHIDE**, $Cr_2S_3 = 201$.—This compound may be obtained in black shining scales, resembling plumbago in appearance, when the vapour of carbonic bisulphide is passed over chromic oxide strongly heated in a porcelain tube. The attraction of chromium for sulphur is but slight: if ammonic hydric sulphide be mixed with a chromic salt, the hydrated sesquioxide of the metal is precipitated, whilst sulphuretted hydrogen is evolved.

(897) **NITRIDE OF CHROMIUM**, Cr_3N_4?: Schrötter.—If the anhydrous violet chromic chloride be heated in a current of dry ammoniacal gas, ammonic chloride sublimes, whilst the chromic chloride is decomposed, emitting a purple light, and an insoluble chocolate-brown compound of chromium and nitrogen is left. If it be heated to between 150° and 200° (302° and 392° F.) in a current of oxygen, it takes fire and burns with a beautiful red light into chromic oxide, emitting nitrogen gas mixed with red fumes of peroxide of nitrogen.

(898) **CHROMIC SULPHATE**; $Cr_23SO_4 = 393$.—There are three varieties of this salt. One of them is a *green* compound,

which is freely soluble in alcohol, but does not crystallize. It is regarded by Siewert as a mixture of a basic and an acid sulphate (*Ann. Chem. Pharm.*, 1863, cxxvi. 95). It may be obtained by boiling hydrated chromic oxide with sulphuric acid. A second modification, of a *violet* colour, may be procured by digesting 8 parts of the hydrated sesquioxide dried at 100° (212° F.) with 9 parts of oil of vitriol, in a shallow vessel exposed to the air at ordinary temperatures. The mixture absorbs water gradually, and becomes converted in two or three weeks' time into a greenish-blue mass of crystals: if these crystals are dissolved in water they form a blue liquid from which alcohol separates the salt in small octahedra containing $15OH_2$. This modification forms with potassic or ammonic sulphate a beautiful violet double salt (chrome-alum) which crystallizes by spontaneous evaporation in large octahedra, corresponding in form and composition to ordinary alum, the formula of the potassium-salt being $K_2Cr_24SO_4.24OH_2$, density 1·826. The solution of the violet sulphate, when boiled, becomes green; and if the crystals of chrome-alum be dissolved in water, and the solution be boiled, the plum-coloured liquid also becomes green, and loses the power of crystallizing unless it be exposed to the air for a long time, or a crystal of an alum be introduced into the liquid. If the violet sulphate be heated to 100° (212° F.) it melts in its water of crystallization, loses $10OH_2$, and becomes converted into the green salt: but if the temperature be raised to about 370° (698° F.), both the green and the violet modification are rendered anhydrous, and a third salt is obtained in *red* crystals, which are no longer soluble in water, or even in concentrated acids, or aqua regia. If digested for a long time with water, however, it becomes converted into the soluble form (Schrötter, *Pog. Ann.*, 1841, liii. 513). The composition of these three sulphates would be represented as follows:

Red insoluble sulphate . . .	Cr_23SO_4
Green soluble sulphate . . .	$Cr_23SO_4.5OH_2$
Violet soluble sulphate . . .	$Cr_23SO_4.15OH_2$.

Several chromic subsulphates may also be formed.

(899) **CHROMIC NITRATE**, or *Nitrate of chromium*, Cr_26NO_3, is a very soluble salt of a green colour; when gently ignited, it loses its acid, and yields a brown oxide of chromium, CrO_2, which has been regarded as a chromate of sesquioxide of chromium; $Cr_2O_3.CrO_3 = 3CrO_2$.

(900) **CHROMIC OXALATES.**—Ammonic oxalate gives a green insoluble precipitate when mixed with a solution of green chromic chloride, but if

the hydrated chromic oxide be digested with oxalic acid, a green soluble oxalate is formed.

Chromic oxalate forms two remarkable series of double salts, viz., *dark blue* salts, which form bluish-green solutions in water, with the general formula $M'_6Cr'''_2 6C_2O_4$, and *garnet-coloured* salts, which form cherry-red solutions in water, of the formula $M'_2Cr'''_2 4C_2O_4$. The *blue potassium salt*, $K_6Cr'''_2 6C_2O_4 6OH_2$, may be obtained by boiling a solution of 19 parts of potassic dichromate, 23 of potassic oxalate, and 55 of crystallized oxalic acid: the chromic acid is reduced to the state of sesquioxide, and carbonic anhydride is evolved in abundance; $K_2Cr_2O_7 + 2K_2C_2O_4 + 7H_2C_2O_4 = K_6Cr'''_2 6C_2O_4 + 6CO_2 + 7OH_2$. The solution is evaporated to dryness, redissolved in water, and set aside to crystallize. The salt is deposited in large rhombic prisms which appear to be black by reflected light, and blue by transmitted light; they appear greenish when powdered. The solution is red by transmitted and green by reflected light: ammonia does not precipitate chromic oxide from the solution, and potassic hydrate occasions no precipitate until the liquid is boiled. Corresponding salts may be obtained containing sodium, ammonium, barium, strontium, calcium, and magnesium instead of potassium, but these different salts vary in the proportion of water which they retain.

The *red potassic salt*, $K_2Cr'''_2 4C_2O_4.8OH_2$, or $12OH_2$, may be prepared by adding 55 parts of oxalic acid to a boiling concentrated solution of 19 parts of potassic dichromate, carbonic anhydride being expelled:

$$K_2Cr_2O_7 + 7H_2C_2O_4 = K_2Cr'''_2 4C_2O_4 + 6CO_2 + 7OH_2.$$

It crystallizes on spontaneous evaporation in small rhomboidal tables, which are dark red both by reflected and by transmitted light: the salt requires about 10 parts of cold water for solution, but is soluble to almost any extent in boiling water. The concentrated solution is dark-green or nearly black by reflected light, but red by transmitted light. Potassic hydrate gives no precipitate in the solution until it is boiled; neither does ammonia cause any separation of chromic oxide. An analogous salt may be formed with ammonium, $(NH_4)_2Cr'''_2 4C_2O_4.8OH_2$.

(901) **Characters of the Compounds of Chromium:**

1.—*The chromous salts*, or *salts of the protoxide*, are but little known. They absorb oxygen rapidly from the air; they are sparingly soluble in water, and form either red or blue solutions, which, like those of the ferrous salts, absorb nitric oxide in large quantity, and form dark-brown solutions. With the chromous salts, *potassic hydrate* gives a brown precipitate of hydrated chromous oxide; *ammonia*, a greenish-white precipitate, which, if ammonic chloride be present, is redissolved by excess of ammonia, forming a blue liquid, which becomes red as it absorbs oxygen. With *potassic hydric sulphide* they give a black sulphide: and with *potassic ferrocyanide* a greenish-yellow precipitate. These salts reduce solutions of gold to the metallic state, and convert corrosive sublimate into calomel.

2.—The *chromic salts*, or *salts of the sesquioxide*, have a sweetish astringent taste, and are poisonous; their solutions redden litmus. They are either green, red violet, or blue-violet coloured; the latter being of the kind of which chrome-alum is

the type; the green solutions generally transmit a red light; these green salts are quickly transformed into the red-violet modification by the addition of a little potassic nitrite, and then slowly pass into the blue-violet modification. With *ammonia* they yield a bulky gelatinous precipitate of hydrated chromic oxide. *Potassic* and *sodic hydrates* give a green precipitate, which is dissolved with a green colour in excess of the cold alkaline solution, but is re-precipitated completely by boiling the liquid, carrying down alkali with it. The *carbonates of the alkali-metals* give a green precipitate which is redissolved by an excess of the alkaline liquid. *Sulphuretted hydrogen* gives no precipitate. The *sulphides of the alkali-metals* precipitate the green chromic oxide, with escape of sulphuretted hydrogen. If any of these precipitates be fused with a mixture of nitre and potassic carbonate, it yields a yellow soluble potassic chromate.

3.—*The Chromates.—Before the blowpipe* in the reducing flame they colour borax and microcosmic salt green. When boiled with dilute sulphuric acid, to which a little alcohol or sugar has been added, they are decomposed, the chromic acid being reduced to the green chromic sesquisulphate; on adding an excess of ammonia, the chromic oxide is precipitated with its characteristic colour. An alcoholic tincture of guaiacum, 1 of resin to 100 of spirit, is turned blue by a very minute trace of free chromic acid (1 millionth part, Schiff), but the colour speedily disappears; an excess of sulphuric acid favours the reaction, which, although exceedingly delicate, is not characteristic, as it is produced by other oxidizing agents. Most of the chromates are strongly coloured. Many of them are insoluble in water, but nearly all of them are readily soluble in dilute nitric acid. Their solutions give a yellow precipitate with *lead* salts, a red with *argentic nitrate*, and an orange with *basic mercurous nitrate*: these precipitates are soluble in nitric acid, but not in acetic acid. When heated with oil of vitriol, the chromates evolve oxygen, whilst with hydrochloric acid they evolve chlorine; in both cases green chromic salts are formed. Workmen engaged in the manufacture of potassic dichromate are liable to the gradual destruction of the nasal bones, and to the occurrence of ulceration of the throat, in appearance a good deal resembling that occasioned by secondary syphilis. Small doses of corrosive sublimate have been found to act as an effectual remedy in such cases (Crace Calvert).

(902) **Estimation of Chromium, and Separation from the Alkalies and Alkaline Earths.**—Chromium can be most accurately estimated in

the form of sesquioxide. It may be easily reduced to this condition, even if it exist in solution in the form of a chromate, by acidulating with hydrochloric acid, and passing a current of sulphuretted hydrogen: the liquid must then be boiled, and on the addition of ammonia to the hot solution, the sesquioxide is precipitated. It is to be well washed, and ignited in a covered platinum crucible; 100 parts of the anhydrous oxide contain 68·63 of chromium. The presence of acetic acid prevents the precipitation of chromic oxide from its solutions by the addition of ammonia, even after long boiling.

The *separation of chromium from the metals of the earths, and from zinc, cadmium, cobalt, nickel, and iron* may be effected by fusing the mineral, or the precipitate obtained by ammonia from its solution in an acid, with a mixture of potassic carbonate and nitre; the chromium is thus converted into a soluble chromate from which the chromium may be precipitated as directed in the foregoing paragraph, whilst the earths and the other metals remain in the insoluble portion either in the form of oxides or of carbonates.

§ VI. MANGANESE: Mn=55.

(903) **MANGANESE**: *Density*, 8·013; *Dyad as in Manganous Salts*, $MnCl_2$; *sometimes Tetrad, as in Manganic Oxide*, MnO_2; *rarely Pseudo-triad as in Manganic Salts*, $Mn_2(SO_4)_3$.—The ores of this metal are tolerably abundant, and it enters, in greater or less quantity, into the composition of a vast number of minerals, so that it is widely diffused throughout the mineral kingdom. The most important and valuable ore of manganese is the black oxide, which occurs either massive or in radiated crystals.

Manganese was first recognized as a distinct metal by Gahn in 1774. It is reduced to the metallic state with difficulty. The best method consists in mixing manganous carbonate with oil and sugar to a paste, and introducing it into a crucible lined with charcoal, and furnished with a cover which should be luted on: it must be heated gently at first, to expel the volatile matters, and then ignited intensely for a couple of hours in the heat of a forge. It may thus be obtained in the form of a metallic globule which contains a variable quantity of carbon; the carbon may be removed by fusing the metal a second time in a porcelain crucible with a little manganous carbonate. It may be prepared from the fluoride by the action of sodium, as in Deville's process for the reduction of aluminium: a solution of manganous chloride also yields plates of the reduced metal when subjected to electrolysis. For a method of preparing metallic manganese on a large scale, see Hugo Tamm, *Chem. News*, 1872, xxvi. 111.

Manganese is of a greyish-white colour, and is brittle, but hard enough to scratch steel; it is very feebly magnetic. By

exposure to the air, it speedily becomes oxidized; it decomposes water slowly at ordinary temperatures, and should be preserved either in sealed tubes or under naphtha.

Manganese when fused with carbon and silicon enters into combination with them: the carbide, when treated with acids, leaves part of the carbon as a black powder: the compound of manganese with silicon is only decomposed with difficulty even by aqua regia, leaving a residue of silica. From the researches of Troost and Hautefeuille (*Compt. Rend.*, 1875, lxxx. 964; and lxxxi. 264), both the carbide and the silicide of manganese would appear to be true compounds and not merely solutions of the non-metals in the metal. A *boride of manganese* is formed in small violet-grey crystals on heating manganese carbide, Mn_3C, with boric acid in a carbon crucible.

Metallic manganese is not employed as such in the arts. It yields various alloys, but none of them are of practical importance, with the exception of its combination with iron, which is harder and more elastic than iron alone. The chief uses of the compounds of manganese are chemical, the black oxide being extensively employed to decompose hydrochloric acid in the preparation of chlorine. It likewise supplies the chemist with his cheapest source of oxygen, and is employed as a colouring material in the manufacture of glass and enamels. It is also used as a flux in the preparation of cast steel; and it furnishes a useful mordant to the calico-printer, when precipitated upon the fibre in the form of brown hydrated oxide.

(904) **CHLORIDES OF MANGANESE.**—Two chlorides of this metal may be obtained: manganous chloride, $MnCl_2$, and manganic chloride, Mn_2Cl_6: the tetrachloride, $MnCl_4$, is also known in solution.

(905) **MANGANOUS CHLORIDE**; $MnCl_2.4OH_2 = 126 + 72$; *Density*, 2·01—This substance is obtained abundantly as a waste product in the preparation of chlorine, by acting on the black oxide of the metal with hydrochloric acid: the chlorine escapes, and manganous chloride is dissolved.* This solution is evaporated

* Various attempts have been made to economize the vast quantities of manganous chloride formed during the manufacture of chloride of lime. One of the most successful until the introduction of Weldon's process (p. 24), was the method employed by Mr. Dunlop. It consists in precipitating the manganese as carbonate, and roasting the carbonate at a temperature of about 320° (608° F.). At Dieuze, in France, a process for the recovery of the waste manganese has been combined with one for turning the tank waste in the manufacture of sodic carbo-

to dryness, redissolved in water, and about one-fourth of the liquid is precipitated by means of sodic carbonate. The impure manganous carbonate thus obtained, after it has been well washed, is boiled with the remainder of the solution, whereby the whole of the iron is precipitated in the form of hydrated sesquioxide, whilst manganous oxide takes its place, and carbonic anhydride is expelled, leaving a solution of manganous chloride free from all metallic impurities except cobalt and nickel. A still better process consists in concentrating a solution of the crude chloride by evaporation, so as to expel the excess of acid, and afterwards diluting with water. A current of sulphuretted hydrogen is then passed through the solution, by which the iron is reduced to the state of ferrous salt; the iron, nickel, and cobalt may then be removed by suspending freshly precipitated

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nate to account, by extracting from it a considerable proportion of its sulphur (p. 450), and the results are said to be very satisfactory.

The following is an outline of the method, given by Mr. J. L. Bell (*Chem. News*, Sept. 27, 1867):

The acid liquor from the chlorine stills having been neutralized (by a process hereafter to be described), but still retaining the chlorides of manganese and iron, is mixed in suitable proportions with the soda waste. In a short time the metallic chlorides become converted into sulphides, by the action of the calcic sulphide, whilst soluble calcic chloride is formed, much of which drains away: $MnCl_2 + CaS = MnS + CaCl_2$. The solid residue is then removed from the tank and exposed to the atmosphere, turning it over from time to time to expose fresh surfaces to the air. The temperature of the mass rises gradually, owing to the absorption of oxygen, which must be moderated by keeping the materials moist. During this process the metallic sulphides are converted into hydrated oxides, whilst the sulphur at the moment of its liberation enters into combination with a portion of calcic sulphide, converting it into a persulphide: meanwhile the liberated oxides act upon a fresh portion of calcic sulphide, lime is set free, and the metals, whether iron or manganese, are reconverted into sulphides: these sulphides again become oxidized by further absorption of oxygen from the air, and the same cycle of changes is renewed as long as any unaltered calcic sulphide remains. Some calcic thiosulphate (hyposulphite) is formed at the same time. These changes may be illustrated by the following equations:

$$4MnS + CaS + 2O_2 = 4MnO + CaS_3; \quad \text{and } MnO + CaS = MnS + CaO;$$

(Calcic thiosulphate.)

$$\text{and } 2CaS + 2O_2 = \overbrace{CaS_2O_3} + CaO.$$

The calcic polysulphide and thiosulphate are freely soluble, and are separated by lixiviation, forming a deep yellow liquid. The insoluble refuse is thus obtained destitute of offensive qualities, and it is stated that it may be kept without creating any nuisance in the neighbourhood. According to an analysis of it given by Mr. Bell, it contains a mixture of about 21 per cent. of lime, 66 of calcic sulphate, with a little carbonate, and about 9 per cent. of oxides of iron, manganese, and aluminium.

Meantime the sulphur is precipitated from the yellow liquor by the waste acid solution of manganous and ferric chlorides from the chlorine stills. This

manganous sulphide in water, and adding it to the liquid as long as the fresh portions of sulphide become blackened; the manganese displaces the other metals from their solution, and they are precipitated as black hydrated sulphides: for example, $FeCl_2 + MnS.xOH_2 = MnCl_2 + FeS.xOH_2$. Kolbe states that pure manganous chloride may be obtained by evaporating to dryness the solution of manganese ore in hydrochloric acid, gently igniting in a Hessian crucible, and exhausting the residue with water; on evaporation, the manganous chloride crystallizes in plates with $4OH_2$; these are of a delicate pink colour, and slightly deliquescent. When heated they leave the anhydrous chloride, $MnCl_2$, which is soluble in alcohol; from this solution it crystallizes with 4 molecules of alcohol, $MnCl_2.4C_2H_6O$.

(906) **MANGANIC CHLORIDE,** Mn_2Cl_6, may be obtained in solution by acting on manganic seequioxide with cold hydrochloric acid: it is of a dark brown colour, and must be concentrated by evaporation *in vacuo*. It is converted by heat into $2MnCl_2 + Cl_2$.

(907) **MANGANIC TETRACHLORIDE,** $MnCl_4$.—An ethereal

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liquor is added until the precipitated sulphur begins to show a black tinge from precipitation of ferric sulphide, which happens as soon as all the free acid is neutralized, the sulphur being precipitated in consequence of the following reaction:

$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 3OH_2 + 6S_2.$$

The precipitated sulphur is then removed from the liquid, and the greater portion of the liquor which it still retains is removed by pressure. It is then dried at a gentle heat, and used for producing sulphuric acid.

The liquor thus rendered neutral still contains the iron and manganese, and is in a fit state for admixture with the soda waste as already described. From the surplus neutral liquors, after a sufficient quantity has been employed in the recovery of the sulphur, the manganese is obtained as follows:—The yellow sulphuretted lime liquor is added to the metallic chlorides, so long as it occasions a precipitate of black ferric sulphide, this is collected and dried: from the mode of its preparation it always contains free sulphur, and may be burned in kilns for making sulphuric acid; oxide of iron remaining.

The iron having been thus separated from the metallic solution a fresh quantity of the yellow liquor is added, and the whole of the manganese thrown down as sulphide, mixed with free sulphur. This precipitate, after drying, is also burned, and the sulphur converted into sulphuric acid. The burnt residue in this case consists of a mixture of the lower oxides of manganese with manganous sulphate. The oxides being free from iron are sold to the glassmakers, after the sulphate has been removed by washing. The concentrated solution of manganous sulphate thus obtained is mixed with an equivalent amount of sodic nitrate; and, when heated, the mixture becomes decomposed. Nitrous fumes are evolved, and are directed into the leaden chambers, whilst the residue consists of a mixture of sodic sulphate with oxide of manganese, containing from 60 to 70 per cent. of the binoxide: $MnSO_4 + 2NaNO_3 = Na_2SO_4 + MnO_2 + 2NO_2$. The sodic salt is removed by washing, after which both it and the oxide of manganese may be applied to their ordinary uses.

solution of this compound of a beautiful green colour is obtained on passing hydrochloric acid gas into a well-cooled mixture of the dioxide with ether.

An *oxychloride* (the *perchloride*, Mn_2Cl_7? of Dumas) is obtained by dissolving potassic permanganate in sulphuric acid, and adding fused sodic chloride in small portions at a time; care is requisite in performing this operation, as if the temperature be allowed to rise too high the mixture sometimes explodes with violence: it is a greenish-yellow gas, which condenses at $-18°$ ($-.0°.4$ F.) to a greenish-brown liquid. The fumes in a moist air assume a purple colour from the formation of permanganic acid: water decomposes it instantly, forming a red solution of permanganic and hydrochloric acids. It is probable that this compound is an oxychloride of the metal, somewhat analogous to the so-called chlorochromic acid (895).

Fluorides of manganese, corresponding to each of these chlorides, have been formed.

(908) **OXIDES OF MANGANESE.**—Manganese forms several compounds with oxygen. The protoxide, MnO, is a powerful base; the sesquioxide, Mn_2O_3, is feebly basic; the red oxide, a compound of these two, $MnO.Mn_2O_3$, appears to be indifferent to the action of acids: so also is the binoxide or black oxide, MnO_2: but the two higher oxides have well-marked acid characters. The general formula for the salts of manganic acid is M'_2MnO_4, and for those of permanganic acid, $M'_2Mn_2O_8$. Neither of the anhydrides of these acids, however, have been obtained.

(909) **MANGANOUS OXIDE,** or *Protoxide of manganese*, $MnO=71$, can be easily obtained by igniting manganous carbonate, or any of the higher oxides of the metal, in a current of hydrogen: it is of an olive-green colour, and unless it has been strongly heated, absorbs oxygen from the air; if ignited in the air it burns, and is converted into a brown oxide. It may be obtained as a white hydrate, MnH_2O_2, by decomposing a manganous salt by any alkali, but it immediately begins to absorb oxygen from the air, and turns brown. It is soluble in ammonia, especially if the solution contains an ammoniacal salt. The protoxide, by its action upon acids, readily forms salts, which are of a pale rose colour; they are neutral to litmus.

(910) **MANGANIC SESQUIOXIDE,** or *Sesquioxide of manganese*; $Mn_2O_3=158$; *Density*, 4·82.—This oxide is found in its anhydrous form in acute square-based octahedra, constituting *braunite*; it occurs naturally in a hydrated state in *manganite* ($Mn_2O_3.OH_2$; *density* 4·35), which is of a blackish-brown colour, and forms brilliant right rhombic prismatic crystals. Manganic oxide may be obtained as a brown hydrate, by passing chlorine, not to saturation, through manganous carbonate suspended in water, and afterwards removing the excess of the carbonate by

means of dilute nitric acid: it is, however, often mixed with hydrated dioxide. Sulphuric acid dissolves it slowly if a portion of the protoxide be present, and a deep red solution is formed; hydrochloric acid in the cold also forms a soluble compound with it: if these solutions be heated they are decomposed, and a manganous salt is the result. When ignited, the sesquioxide loses one-eighth of its oxygen, and leaves the red oxide. The manganic salts, or salts formed from the sesquioxide, are isomorphous with those of alumina and ferric oxide. It appears to be the manganic oxide that imparts the violet colour to glass to which the black oxide has been added, and the colour of the amethyst is also said to be due to this oxide.

(911) **MANGANIC DIOXIDE**, *Binoxide, Deutoxide,* or *Peroxide;* $MnO_2=87$; *Density,* 4·94; *Comp. in* 100 *parts,* Mn, 63·22; O, 36·78.—This oxide is the black manganese of commerce, and the *pyrolusite* of mineralogists; it is found in steel-grey rhombic prisms. *Psilomelane* is a black stalactitic or amorphous variety, frequently mixed with one of the lower oxides of the metal. *Varvicite* ($Mn_2O_3.2MnO_2.OH_2$; *density* 4·53) is the name given to a hard lamellated crystalline hydrate, found by Phillips at Hartshill, in Warwickshire. *Wad* is also a hydrated dioxide of manganese, with a variable amount of water; it is in a less compact form than psilomelane, and is of a brown colour. Small quantities of cobalt and of the carbonates and nitrates of the metals of the earths are frequent constituents of these ores.

Manganic dioxide is a good conductor of electricity, and is strongly electronegative in the voltaic circuit. When mixed with acids, it furnishes a valuable oxidizing agent. When ignited, it gives off one-third of its oxygen, and the red oxide is left; $3MnO_2=Mn_3O_4+O_2$: if heated with concentrated sulphuric acid, half its oxygen escapes, and manganous sulphate is formed; $2MnO_2+2H_2SO_4=2MnSO_4+2OH_2+O_2$. With hydrochloric acid, chlorine is abundantly evolved, and manganous chloride is left. Nitric acid has but little effect upon it. Manganic dioxide is precipitated in a hydrated form as a reddish-brown powder, $MnO_2.OH_2$, when potassic manganate or potassic permanganate is decomposed by an acid. When the red oxide is treated with nitric acid, a black hydrated dioxide is left, containing $4MnO_2.OH_2$. The same hydrate is probably formed on adding a solution of chloride of lime to a neutral solution of manganous sulphate or chloride. From the recent researches of Fremy (*Compt. Rend.,* 1876, lxxxii. 1231), manganic oxide, MnO_2, would

appear to be capable of forming salts with sulphuric acid, but these compounds are entirely decomposed by water with precipitation of a manganic hydrate, $MnO_2.2OH_2$.

(912) **Commercial Assay of Oxide of Manganese.**—The commercial value of black oxide of manganese depends upon the proportion of chlorine which a given weight of it will liberate when it is heated with hydrochloric acid. This quantity of chlorine varies much in different samples, and is dependent upon the proportion of oxygen which the oxide of manganese contains in excess of that which is necessary to form the protoxide. A convenient method of estimating this excess of oxygen is founded upon the circumstance that the black oxide of manganese is decomposed in the presence of oxalic acid and free sulphuric acid, manganous sulphate is formed, and all the excess of oxygen reacts upon the oxalic acid, and converts it into carbonic anhydride, which is evolved. If the mixture be weighed before the decomposition is effected, and again after it has been completed, the loss will indicate the amount of carbonic anhydride; and from this the available amount of oxygen is readily calculated. The reaction may be traced thus: $MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2CO_2 + 2OH_2$. Each molecule of manganic dioxide gives 2 molecules, or almost exactly its own weight, of carbonic anhydride.

The apparatus of Will and Fresenius (fig. 342, p. 431), is well adapted to the performance of this experiment: 5 grams of the oxide of manganese to be tested, are reduced to an extremely fine powder, and mixed with 15 grams of neutral potassic oxalate; the mixture is placed in the flask *a*, and about 60 c. c. of water is added: the experiment is then proceeded with exactly as in the method already described for estimating carbonic anhydride in a carbonate (611). The decomposition of the ore is known to be complete as soon as all the black particles have disappeared.

If the sample of oxide of manganese contain a carbonate of any of the earths, as may be readily ascertained by the effervescence which will be occasioned on moistening a portion of the oxide with dilute nitric acid, it will be necessary to remove this carbonate. This is easily done by washing the weighed portion into the flask itself with nitric acid diluted with from 16 to 20 parts of water; as soon as the effervescence has ceased, and the oxide has been allowed to subside, the acid liquid must be carefully poured off, and the flask filled up once or twice with distilled water; in order to retain any suspended particles, the washings may be thrown upon a small filter, which is afterwards introduced into the flask, and the experiment is then proceeded with as usual.

(912*a*) **RED OXIDE OF MANGANESE;** $Mn_3O_4 = 229$; *Comp. in* 100 *parts,* Mn, 72·05; O, 27·95.—This oxide corresponds to the black oxide of iron; it is formed by igniting any of the oxides of manganese in the open air: it occurs native in *hausmannite* (*density* 4·72) either massive or in four-sided pyramidal crystals of a black colour. The oxide is soluble in phosphoric and in sulphuric acid, but does not form definite salts with either of them.

(913) **MANGANIC ACID;** $H_2MnO_4 = 121$.—When equal weights of potassic hydrate and finely levigated manganic dioxide are fused together, a substance is formed which, when dissolved in a small quantity of water, has a green colour, but when

largely diluted, becomes purple, and ultimately claret-coloured, whilst a precipitation of hydrated manganic dioxide takes place. This substance, owing to these changes of colour, has been long known under the name of *mineral chameleon.* The green colouring material is potassic manganate, K_2MnO_4, an unstable compound, which readily parts with oxygen, or absorbs a larger amount of it, in the latter case forming a red compound; hence the changes of colour produced.

Manganic acid undergoes rapid spontaneous decomposition unless it be in combination with some powerful basyl. A tolerably stable manganate may be obtained by heating finely powdered dioxide of manganese with its own weight of caustic potash, soda, or baryta. Béchamp heats an intimate mixture of 10 parts of finely powdered black oxide of manganese with 12 of potassic hydrate, dries it in an iron dish, and heats the porous residue to dull redness in an earthen retort, into the tubulure of which a green glass tube is luted; he then passes a current of pure dry oxygen over the mixture as long as it is absorbed. If the green mass thus obtained be treated with a small quantity of cold water, it is partially dissolved, forming a green solution, from which potassic manganate may be obtained in the crystalline state by evaporating it in a vacuum over sulphuric acid. These crystals are isomorphous with the corresponding sulphates and chromates. Potassic manganate, K_2MnO_4, is anhydrous, and is immediately decomposed by water into the permanganate, potassic hydrate, and manganic dioxide; it is readily soluble, however, in water containing free alkali. Sodic manganate is prepared on a large scale by Mr. Condy, by exposing a mixture of caustic soda and finely powdered oxide of manganese to a dull red heat in shallow vessels for 48 hours; 7 cwt. of oxide of manganese are mixed with the alkali obtained from $1\frac{1}{2}$ ton of soda-ash.

Manganates.—The manganates are very unstable, their solutions being decomposed by ebullition. A small quantity of any free acid changes the colour of their solutions from green to red, owing to the formation of a permanganate, and of a manganous salt: for instance, $5K_2MnO_4+4H_2SO_4$, gives $2K_2Mn_2O_8+MnSO_4+3K_2SO_4+4OH_2$. Organic matter also readily abstracts oxygen from them so that their solutions cannot be filtered through paper. In the solid form they are readily decomposed by elevation of temperature, with evolution of oxygen, but an excess of alkali renders the salt more stable. Sulphurous and hypophosphorous acids readily, and phosphorous acid more

slowly, reduce the manganates to manganous salts: the following equation represents the result with sulphurous acid;

$$K_2MnO_4 + 2H_2SO_3 = MnSO_4 + K_2SO_4 + 2OH_2.$$

Manganic acid has a very intense colouring power: this fact enables us to detect manganese in very minute quantity before the blowpipe; the material supposed to contain it is fused upon platinum foil with a little potassic or sodic carbonate: if any trace of manganese be present, a green colour is imparted to the fused mass.

(914) **PERMANGANIC ACID**; $H_2Mn_2O_8 = 240$.—If a solution of potassic manganate be largely diluted with water, the colour changes from green to violet; the manganic acid passes to a higher state of oxidation, and potassic permanganate is formed.

This salt may be prepared by mixing intimately 4 parts of finely powdered dioxide of manganese with $3\frac{1}{2}$ of potassic chlorate; 5 parts of potassic hydrate are dissolved in a small quantity of water, and added to the mixture, which is dried and reduced to powder, and then heated to dull redness for an hour in an earthen crucible. When cold, the mass is treated with water, and filtered through a funnel plugged with asbestos; the solution, after being neutralized with sulphuric acid, and concentrated by evaporation, yields beautiful red acicular crystals of *potassic permanganate*, $K_2Mn_2O_8 = 316{\cdot}2$. If a current of carbonic anhydride be passed through a solution of manganate, prepared by Béchamp's process, until the green colour has been changed to red, and the clear liquid decanted from the precipitated oxide of manganese, very fine crystals of the permanganate are obtained on evaporation; $3K_2MnO_4 + 2CO_2 = K_2Mn_2O_8 + 2K_2CO_3 + MnO_2$. A still better process is to pass chlorine through the solution, $2K_2MnO_4 + Cl_2 = K_2Mn_2O_8 + 2KCl$. The crystals of the permanganate which are isomorphous with those of potassic perchlorate, require about 16 parts of cold water for solution. When potassic permanganate is heated, it is first converted into the manganate and then into a black powder, having the composition, $K_2Mn_2O_5 = K_2O + 2MnO_2$.

Potassic permanganate is in many cases a useful oxidizing agent: it may be employed to detect the presence of sulphurous acid in solution in sulphuric or hydrochloric acid; sulphurous acid quickly deoxidizes it, and destroys its colour if present. Neutral solutions of the sulphides and the pentathionates quickly

discharge the colour of a solution of potassic permanganate, and a similar effect is produced by acid solutions of the sulphates, thiosulphates (hyposulphites), tetrathionates, sulphocyanides, and nitrites. The trithionates produce the same effect, but more slowly. Acidulated solutions of the mercurous, ferrous, stannous, and antimonious salts, and acid solutions of arsenites, likewise decolorize a solution of permanganate rapidly, a manganous salt being formed. A solution of this salt constitutes a test-liquid which may be very usefully employed in many cases of volumetric analysis, as already exemplified in the instance of the ores of iron (883).

Permanganates.—The permanganates are much more stable than the manganates, and their solutions may be boiled without undergoing decomposition, either alone or in the presence of small quantities of the alkalies: boiling with a concentrated solution of potassic hydrate, however, converts them into manganates. Organic matter, moreover, combines with part of the oxygen contained in the acid, and reduces it first to manganic acid and then to the dioxide of the metal, which is precipitated as a hydrate: their solutions, therefore, must not be filtered through paper, but through a funnel loosely plugged with asbestos. A dilute solution of the permanganate of known strength is sometimes employed to roughly estimate the amount of organic impurity in waters supplied for domestic use. When the permanganates are ignited, oxygen is given off, and a manganate is reproduced, and this, if the heat be too great, is in turn decomposed with a further evolution of oxygen. Most of the permanganates are freely soluble in water, argentic permanganate being the least soluble of the salts. If concentrated solutions of potassic permanganate and argentic nitrate be mixed together, a red crystalline argentic permanganate is deposited. It may be employed for the preparation of the other permanganates; if it be levigated with water, and mixed with a solution of the chloride of the metal of which the permanganate is required, double decomposition occurs, and argentic chloride is formed, whilst the desired permanganate is obtained in solution. In this way baric permanganate may be procured, and from it the permanganic acid may be obtained in solution, by the cautious addition of dilute sulphuric acid as long as any precipitate is produced: on evaporation a brown crystalline mass is left, which is very soluble in water; the solution is decomposed by a slight elevation of temperature: at about 40° (104° F.) hydrated manganic dioxide

is deposited, and oxygen gas escapes. Terreil prepares the acid by distilling potassic permanganate with slightly diluted sulphuric acid.

Condy has employed solutions of potassic manganate, and potassic permanganate, as disinfecting agents, for which purpose they are admirably adapted: the organic matter is rapidly and completely oxidized by their means, and as the solutions have no corrosive action, and no ill-odour of their own, solutions of these salts form valuable local applications to fœtid sores.

(915) **MANGANOUS SULPHIDE**, or *Protosulphide of manganese*, $MnS.xOH_2$, is obtained as a yellowish-red hydrate, by precipitating a manganous salt by ammonic hydric sulphide: the sulphide under certain circumstances has a sulphur-yellow colour, and has also been obtained green and crystalline, and of a violet hue (Clermont and Guiot, *Bull. Soc. Chem.*, 1877, [2], xxvii. 353). The presence of traces of iron, cobalt, or nickel renders it black: it speedly becomes oxidized by exposure to the air. A crystalline sulphide may be obtained in black rhombic prisms, by heating the hydrated sesquioxide in the vapour of carbonic bisulphide; native manganous sulphide is occasionally met with, as *manganese blende*, or *alabandine*, of a brownish-black or steel-grey colour, and feeble metallic lustre. The other sulphides of manganese have not been accurately examined.

(916) **MANGANOUS SULPHATE** ($MnSO_4.5OH_2 = 151 + 90$; *Density, anhydr.* 3·1) is obtained for the use of the calico-printer, by digesting the dioxide in dilute sulphuric acid, in order to remove the carbonates, then heating it with oil of vitriol, evaporating to dryness, and gently igniting the residue to decompose the ferrous sulphate, which does not resist so high a temperature as manganous sulphate. On digesting the mass, after it has become cool, in water, the manganous sulphate is dissolved, and may be obtained in crystals on evaporation: it crystallizes below 5° (41° F.) with $7OH_2$ in efflorescent prisms; between 7° and 20° (44°·6 and 68° F.) with $5OH_2$; and between 20° and 30° (68° and 86° F.) with $4OH_2$ (Brandes): when crystallized from boiling oil of vitriol it forms an acid salt having the composition $MnH_2(SO_4)_2$. It forms a double salt with potassic sulphate, $MnSO_4.K_2SO_4.6OH_2$, which is isomorphous with the corresponding magnesic sulphate.

MANGANIC SULPHATE is a deep green amorphous powder, but it forms a compound with potassic sulphate which crystallizes in octahedra, $K_2Mn'''_24SO_4.24OH_2$, corresponding in form and composition with common alum.

(917) **MANGANOUS CARBONATE**; $MnCO_3 = 115$.—The anhydrous carbonate forms the native *manganese spar*, and frequently accompanies spathic iron: the artificial carbonate may be obtained as a white hydrate, $MnCO_3.OH_2$, on precipitating manganous chloride by a carbonate of one of the alkali-metals: it gives off half its water over concentrated sulphuric acid, and becomes brownish by drying.

(918) **Characters of the Salts of Manganese.**—The salts formed from the *protoxide*, or manganous salts, are the only salts of manganese of importance: they are of a delicate rose colour, and have an astringent taste. With *potassic* and *sodic hydrates*, their solutions yield a white precipitate of hydrated protoxide, which absorbs oxygen rapidly, and becomes brown by exposure to the air. *Ammonia* gives a similar precipitate, which is soluble in excess of the precipitant, especially when it contains ammonic chloride; the solution absorbs oxygen quickly, and deposits a brown hydrated protosesquioxide. The *carbonates of the alkali-metals* give a white precipitate of manganous carbonate, soluble in ammonic chloride. With *ammonic hydric sulphide* a characteristic flesh-coloured hydrated manganous sulphide is formed, which becomes brown by exposure to the air, and is readily dissolved by hydrochloric or nitric acid; the formation of this precipitate is prevented by the presence of certain organic ammonium salts. *Sulphuretted hydrogen* gives no precipitate in ordinary solutions of manganese, but a neutral solution of manganous acetate is partially precipitated by this reagent. *Potassic ferrocyanide* gives in neutral solutions a white precipitate soluble in acids; and *potassic ferricyanide* a brown precipitate. Mr. Crum has pointed out an extremely delicate test for the presence of a manganous salt, provided that the solution is free from chlorides; the liquid must be mixed with dilute nitric acid, and a little plumbic dioxide added: on boiling the mixture, the red colour of permanganic acid is produced by a trace of manganese which is too small to be otherwise recognized. *Before the blow-pipe*, the compounds of manganese give a very characteristic bluish-green opaque bead with sodic carbonate: a bead of borax or of microcosmic salt becomes violet in the oxidizing flame, if manganese be present; the colour disappears in the reducing flame.

(919) **Estimation of Manganese, and Separation from the Alkalies.**—Manganese is generally estimated in analysis in the form of the red oxide, Mn_3O_4, which contains 72·05 per cent. of the metal. For this purpose it is precipitated from a boiling solution of its salts by potassic or sodic carbonate; the precipitated carbonate is well washed, and then heated to redness, by which the carbonic anhydride is expelled, and the red oxide is produced by absorption of oxygen from the air.

Separation of Manganese from the Alkaline Earths.—The solution must be rendered nearly neutral, and ammonic hydric sulphide added, which precipitates the manganese as sulphide:

the sulphide must then be redissolved in hydrochloric acid, precipitated by potassic carbonate, and the manganese estimated, after ignition, as red oxide. It is apt, however, to retain some portions of the earths when thus separated. The oxide must therefore be again redissolved in hydrochloric acid, ammonic chloride added, and then a mixture of ammonia and ammonic carbonate in excess; the manganese will remain in solution; but if strontium, calcium, or barium be present, they will be precipitated in the form of carbonates, and can be collected on a filter, weighed, and deducted from the weight of the oxide previously obtained.

Separation from Zinc, Cadmium, Cobalt, and Nickel.—The solution is mixed with potassic acetate in excess, to convert the metals into the acetates, then sulphuretted hydrogen is passed; the manganese remains in solution, whilst the other metals are precipitated as sulphides if the solution is only faintly acid. If cadmium alone is present, the addition of potassic acetate is unnecessary.

Separation from Iron, Chromium, Uranium, Aluminium, and Glucinum.—This is readily effected by converting the iron into a ferric salt, diluting the solution largely with water, and digesting it with finely levigated baric carbonate. Manganese alone remains in the liquid, the other oxides being displaced by baryta. The excess of barium is removed by sulphuric acid, and the manganese precipitated by sodic carbonate.

Manganese is connected by isomorphous relations with a great number of the elementary bodies. Its protoxide is isomorphous with the oxides of the magnesian group: its sesquioxide is isomorphous with alumina, and with ferric and chromic oxides. The manganates are isomorphous with the sulphates, and the permanganates with the perchlorates.

CHAPTER XXII.

GROUP VI.

CERTAIN METALS WHICH FORM ACIDS WITH OXYGEN.

Metal.	Symbol.	Atomic weight.	Solid Atomic vol. H=1.	Specific heat.	Fusing point. °C.	Fusing point. °F.	Density.	Electric conductivity at 0° C.
Tin	Sn	118	16·18	0·0562	228	442·4	7·292	12·36
Titanium ...	Ti	50						
Molybdenum	Mo	96	11·14				8·62	
Tungsten ...	W	184	10·45	0·0334			17·60	
Vanadium ...	V	51·3						
Arsenic ...	As	75	13·10	0·0830			5·726	4·76
Antimony ...	Sb	122	18·18	0·0508	450	842	6·71	4·62
Bismuth ...	Bi	210	21·36	0·0308	264	507·2	9·83	1·245

IN this list zirconium, thorinum, niobium, and tantalum are omitted, because so little is known of them. The foregoing list of metals capable of yielding acids with oxygen is divisible into three natural families, which have little in common. (See p. 355.)

§ I. TIN: $Sn^{IV}=118$.

(920) **TIN** (Stannum): *Density*, 7·292; *Fusing-pt.*, 227°·8 (442° F.); *Dyad in Stannous salts as* $SnCl_2$; *Tetrad in Stannic salts, as* $SnCl_4$.—This beautiful metal is one of those which have been longest known to man, as it is mentioned in the Books of Moses. Tin, however, is met with in but few localities. Its only ore of importance is the dioxide, or tin stone, which occurs crystallized in prisms isomorphous with those of rutile. It is usually found in veins, running through primitive rocks of porphyry, granite, or clay-slate, and is generally mingled with the sulphides and arsenides of copper and iron, and frequently also with wolfram. The most celebrated tin mines are those of Cornwall, which were worked before the Roman invasion; they furnish annually upwards of 10,000 tons of the metal: the mines of Malacca also yield a very pure tin, and the metal is likewise obtained to a smaller extent from Mexico and to a large extent from Australia. The tin veins in Cornwall are frequently associated with those of copper, and they run almost invariably east and west. The tin ore is often met with in alluvial soils, whither it has been carried from its original position by the action of

water. In this case the ore occurs in detached, rounded masses, and is very pure, constituting what is termed *stream tin.* The position of the veins is frequently traced by following the stream towards its source, up to the point where the ore ceases to be found; a careful examination of the vicinity generally leads to the discovery of the vein.

(921) **Extraction of Metallic Tin.**—In order to extract the metal from the ore, it is subjected to a series of operations, some of which are of a mechanical and others of a chemical nature. They may be classified thus:

1.—*Stamping and washing,* to remove the earthy and lighter portions. 2.—*Roasting,* to decompose the pyrites and get rid of the arsenic and sulphur. 3.—*Washing,* to dissolve out cupric sulphate, and carry off the ferric oxide. 4.—*Reduction,* by which the tin is separated from the oxygen and the *gangue* or earthy matter. 5.—*Refining,* or liquation, and *boiling* with green wood.

1.—The purer portions of the ore are first picked out by hand; the residue, consisting chiefly of tin-stone, with the earthy impurities of the matrix, mixed with arsenical copper and iron pyrites, passes to the stamping mill, where it is reduced to a coarse powder. This powder is then buddled and washed (556), to remove the lighter impurities.

2.—The heavier portion, however, still retains a considerable quantity of arsenical iron and copper pyrites. The next operation is intended to get rid of these substances; with this view the washed ore is roasted in a reverberatory furnace until the arsenic and a good deal of the sulphur are expelled, and the ore becomes converted into a yellowish-brown powder; this process usually lasts about twelve hours. During this roasting, frequent stirring is necessary in order to expose fresh surfaces freely to the air. By this means the iron pyrites is decomposed, and is converted into sulphurous anhydride and ferric oxide; the arsenic is expelled as arsenious anhydride, and the greater part of the sulphide of copper is converted into cupric sulphate; this conversion is completed by exposing the mass in a moistened state to the air for some days.

3.—The cupric sulphate is then dissolved out by lixiviation; after which the principal part of the ferric oxide, as it is much lighter than the stannic oxide, is got rid of by washing.

4.—The washed ore is now ready for reduction.* In order

* When much wolfram is contained in the ore it is sometimes fused with

to attain this object, it is mixed with from one-fifth to one-eighth its weight of powdered anthracite or charcoal, and with a small proportion of lime to facilitate the fusion of the siliceous gangue, which still remains mingled with the ore. The mixture having been rendered damp, for the purpose of preventing the finer particles from being carried away by the current of air, is introduced into the reducing furnace. This is a reverberatory furnace with a low arch or crown. The charge having been placed upon the hearth, the doors are closed up, and the heat is gradually raised for five or six hours; the stannic oxide is thus reduced by the carbon before the temperature rises high enough to cause the oxide to fuse with the silica, with which it would form an enamel difficult of reduction. Towards the end of the operation the heat is raised until it becomes very intense; the slags are thus rendered fluid, and the reduced metal subsides to the bottom, and is allowed to run off into cast-iron pans, from which it is ladled off into moulds; but the ingots so obtained are by no means pure.

5.—They are therefore next submitted to a process of *liquation*, which consists in heating the ingots to incipient fusion upon the bed of a reverberatory furnace: the purer tin, being the more fusible, gradually melts out and leaves an alloy, which has a higher melting-point. This less fusible portion, when remelted, forms the inferior variety called *block tin*. The tin which has run out of the ingots is drawn off into a second pan in which the metal is gently heated, being kept in a state of fusion by a fire underneath; here it is agitated briskly by thrusting into the mass stakes soaked in water; the steam thus produced, as it bubbles up through the molten metal, carries the dust, slag, and other mechanical impurities to the surface. After this treatment has been continued for about three hours, the metal is allowed to remain undisturbed for a couple of hours; it is then skimmed, ladled out, and cast into ingots for the market. The portion contained in the upper half of the pan is the purest, as owing to the low density of tin, and its tendency to separate from its alloys, it rises to the surface. The finest quality of the metal is frequently heated a second time to a temperature a little short of its melting-point; at this temperature it becomes brittle, and if allowed to fall

sodic carbonate before proceeding to the reduction; the tungstic acid is thus removed in the form of a soluble sodic tungstate, which is extracted by water, and is sometimes employed in calico-printing as a mordant; it has lately also been proposed to apply it to muslin dresses to prevent them from burning with flame, should they happen to take fire.

from a height, it breaks into irregular prismatic fragments, which are known as *dropped* or *grain tin*. The splitting of the mass into these fragments is a rude guarantee of the purity of the metal, since impure tin does not become brittle in this manner.

On the Continent, the stream tin is frequently reduced in small blast furnaces, termed by the French *fourneaux à manche*; the fuel used in this case is charcoal. The tin which is imported from Banca is almost pure. English tin usually contains small quantities of arsenicum, copper, iron, and lead, and often traces of gold.

When required in a state of perfect purity, the metal may be obtained by means of voltaic action. For this purpose a concentrated solution of crude tin in hydrochloric acid may be placed in a beaker, and water cautiously poured in without disturbing the dense solution below. If a bar of tin be plunged into the liquid, beautiful foliated or prismatic crystals of pure tin are gradually deposited on the bar at the point of junction between the metallic solution and the water. Another method consists in covering the outside of a platinum basin with wax, all except a small part of the bottom: it is then placed in a porcelain basin on a piece of amalgamated zinc. The platinum dish is filled with a dilute solution of stannous chloride, and dilute hydrochloric acid (1 acid to 20 water) is then poured into the porcelain basin until it just covers the edge of the platinum dish. In two or three days beautiful crystals of metallic tin will be formed in the platinum basin.

(922) **Properties of Tin.**—Tin is a white metal with a tinge of yellow, and a high metallic lustre. It is rather soft, and is very malleable, but is deficient in tenacity. At a temperature of about 100° (212° F.) its ductility is considerable, and it may then be easily drawn into wire. In a laminated state it is well known as *tinfoil*. If a bar of tin be bent, it emits a creaking sound, a property which it possesses in common with cadmium; if bent several times in succession backwards and forwards, it becomes sensibly hot at the point of flexure. These effects depend upon a mechanical alteration of the relative position of its crystals, and their mutual friction. Tin, when handled, communicates a peculiar odour to the fingers. It is a tolerably good conductor both of heat and electricity. It fuses at 227°·8 (442° F.), according to Crichton, or 233° (451°·4 F.) (Person), but is not sensibly volatilized in the furnace. It may be obtained in crystals by slow cooling after fusion. Tin is but slowly tarnished by exposure to the air and moisture at ordinary temperatures, but if

heated to redness in a current of steam, or if exposed to the air at a high temperature, it becomes rapidly converted into the dioxide and burns with a brilliant white light. Nitric acid of density 1·52 does not attack tin, but if diluted to 1·3 it acts upon it violently, and produces an insoluble hydrated dioxide of the metal known as metastannic acid; at the same time, owing to the decomposition of water, a considerable quantity of ammonia, and probably some hydroxylamine is formed, which enters into combination with the excess of nitric acid. Strong hydrochloric acid, when heated with tin dissolves it gradually with evolution of hydrogen. Aqua regia, if not too concentrated, dissolves the metal and converts it into the tetrachloride. Dilute sulphuric acid is without action on the metal in the cold, but if the concentrated acid be boiled with it, the tin becomes converted into stannic sulphate, and globules of sulphur are separated, whilst sulphurous anhydride escapes: the tin appears in this case to be dissolved as stannous sulphate, which is oxidized to stannic sulphate at the expense of the sulphurous anhydride, and sulphur is deposited; $Sn + 2H_2SO_4$ yielding $Sn''SO_4 + SO_2 + 2OH_2$; and $2Sn''SO_4 + SO_2 + 2H_2SO_4$ furnish $2(Sn^{iv}2SO_4) + S + 2OH_2$. Potassic and sodic hydrates act upon tin at high temperatures, hydrogen being evolved, whilst a soluble metastannate of the alkali metal is formed. Tin combines readily with sulphur, phosphorus, chlorine and bromine, if heated with them.

Owing to its brilliancy, and its power of resisting ordinary atmospheric changes, tin is largely employed for coating other metals which are more oxidizable, in order to protect them during use. Iron and copper are especially adapted to the operation of tinning. In India, tin is applied instead of silver to steel and iron articles by way of ornament; the tin is melted, and while still liquid is agitated in a box until it has become solid; the fine powder thus procured is separated, by suspension in water, from the coarser particles, and is made into a thin paste with glue; it is then applied in the desired pattern; when perfectly dry it is burnished, and afterwards varnished; its brilliancy is thus preserved unchanged.

(923) **Tin-Plate.**—The ordinary process of tinning iron differs from the foregoing one, and is far more important in its economical results. In tin-plate, an actual alloy of the two metals is formed upon the surface of the iron, the external surface being pure tin.

For the manufacture of tin-plate, the best charcoal iron is required. After the iron has been rolled and cut into sheets of suitable thickness and size, their

surface is made chemically clean by immersing them for four or five minutes in a mixture of sulphuric acid and water, after which they are raised to a red heat in a reverberatory furnace; they are then withdrawn, allowed to cool, and hammered flat. In order to detach from them all the scales of oxide, they are passed between polished rollers, and as they emerge they are plunged one by one into a mixture of bran and water which has become sour by exposure to the air; here they remain for some hours, and are thence transferred to a vessel containing a mixture of dilute sulphuric and hydrochloric acids; lastly, they are scoured with bran, and plunged into pure water or lime-water, in which last, if the surface be clean on immersion, they may remain for any length of time without rusting: these preliminary steps are necessary in order to secure a clean surface, as the tin will not adhere to an oxidized or even a dusty plate. In some works, the plates, after they have been scoured, are further cleaned with hydrochloric acid holding zinc in solution, and then dipped into the melted tin in the manner about to be described.

The plates having been prepared by either of the foregoing processes are next plunged one by one into a large vessel of melted tallow free from salt, and after remaining there for an hour they are immersed in the bath of melted tin, which is preserved from oxidation by a stratum of grease three or four inches (8 or 10$^{cm.}$) thick. Here they remain for about an hour and a half; they are then withdrawn and allowed to drain. After this they are plunged into a second bath of pure tin, and the excess of tin is removed by again heating them in a bath of tallow: the tin melts and runs down to the lower edge of the plate; when cool, this thickened margin is finally reduced by dipping the edge of the plate once more into tin kept at a temperature much above its melting-point; the heat quickly fuses the superfluous metal, which is then detached by giving the plate a sharp blow. Tin-plate is sometimes made to exhibit a beautiful crystalline appearance, known under the term *moirée métallique*. A mixture is made of 2 parts of nitric acid, 2 of hydrochloric acid, and 4 of water: the tin-plate is gently heated, and the liquid spread evenly over with a sponge; the crystals gradually appear. The plate is then plunged into water, dried quickly, and varnished. Different coloured varnishes are used to vary the effects.

Tinning copper is the same in principle, but is a simpler operation than the tinning of iron: the surface of the metal is rendered clean by rubbing it, while heated, with sal ammoniac; when quite bright, the copper is sprinkled with a little rosin to prevent oxidation, and melted tin is then poured on and spread over the surface with tow by the workman, who keeps the article constantly at a high temperature; the superfluous tin is wiped off with the tow. The addition to the tin of one-fourth of its weight of lead renders the operation more easy, as the alloy is more perfectly liquefied. Pins, which are made of brass wire, are tinned by boiling them for a few minutes with granulated tin and a solution of 1 part of cream of tartar, 2 parts of alum, and 2 of common salt in 12 parts of water; in the course of a few minutes a brilliant, white, closely adhering coating of tin is deposited upon the surface of the pins.

(924) **Alloys of Tin.**—The alloys of tin which are employed in the arts are numerous. *Britannia metal* is a white alloy which is a good deal used for making teapots and spoons of a low price; it consists of equal parts of brass, tin, antimony, and bismuth. *Pewter* is another alloy of this description; both of these possess considerable malleability, pewter being intermediate in hardness between lead and Britannia metal. The best pewter consists of

4 parts of tin, and 1 of lead. Another alloy, which is intermediate in properties between pewter and Britannia metal, is called *Queen's metal;* it is used for the manufacture of teapots and common spoons. It consists of 9 parts of tin, 1 part of antimony, 1 of bismuth, and 1 of lead. *Plumber's solder* is an alloy of tin and lead which is more fusible than pure lead: *fine solder* consists of 2 parts tin and 1 of lead; *common solder* of equal parts of lead and tin; and *coarse solder* is composed of 2 of lead to 1 of tin. Lead and tin may be melted together in all proportions, and notwithstanding their difference in density, they do not separate when the fused mixture is allowed to cool slowly (Matthiessen). The same is true also of the alloy of tin and zinc; if the two metals be fused together in equal proportions, the result forms a hard, white alloy nearly as tough as brass.

Tin forms several important alloys with copper. *Speculum metal,* used for the mirrors of reflecting telescopes, consists of 1 part tin and 2 copper, or Cu_4Sn: it is of a steel-white colour, extremely hard, brittle, and susceptible of a high polish. The proportions of the constituents of speculum metal recommended by different authorities vary, and sometimes a small quantity of arsenic is added to the alloy. *Bell-metal* consists of about 78 of copper and 22 of tin, or Cu_6Sn: sometimes a mixture of zinc and lead is substituted for a part of the tin. *Gun metal* contains only 9 or 10 per cent. of tin. *Bronze* contains less tin than bell-metal, with usually an addition of 3 or 4 per cent. of zinc. The bronze used for coin consists of 95 parts of copper, 4 of tin, and 1 of zinc. Bronze admits of a peculiar kind of tempering: if it be annealed, and allowed to cool slowly, it becomes hard, brittle, and elastic; but if cooled suddenly, it may be hammered, and worked at the lathe; this property is taken advantage of in the manufacture of articles with this alloy; they are wrought in the soft state, and are afterwards hardened by annealing. The effect of sudden cooling upon bronze is therefore just the reverse of that which is produced by it upon steel. These alloys of copper and tin are much harder than copper itself, and considerably more fusible. The melting-point of copper, according to Daniell is 1091°·1 (1996° F.); but an alloy of tin and copper containing 6·6 per cent. of tin, fused at 921°·1 (1690° F.); and one with 12·3 per cent. of tin, at 834°·4 (1534° F.). These alloys have a density greater than the mean of that of the metals which enter into their composition. They resist oxidation in the air more completely than copper.

An inconvenience in the use of the alloys of copper and tin arises from the circumstance, that, when melted, the two metals, owing to their difference in density, have a tendency to separate from each other, even after they have been well incorporated: the tin accumulates in the upper portions of the melted mass, where it forms a more fusible alloy. It is therefore very difficult in large castings to obtain a mass of metal the composition of which is uniform throughout. A very important and elaborate research on the composition and properties of various kinds of bronze has recently been made by Riche (*Ann. Chim. Phys.*, 1873, [4], xxx. 35).

An *amalgam of tin and mercury* is employed for the silvering of mirrors. In order to apply it to the glass, a sheet of tinfoil is spread evenly upon a smooth slab of stone, which forms the top of a table carefully levelled, and surrounded by a groove for the reception of the superfluous mercury. Clean mercury is poured upon the tinfoil, and spread uniformly over it with a roll of flannel; more mercury is then poured on until it forms a fluid layer of the thickness of about half-a-crown, and the surface is cleared of all impurities by passing a linen cloth lightly over it; the plate of glass is carefully dried, and its edge being made to dip below the surface of the mercury, is pushed forward cautiously so that all bubbles of air are excluded as it glides over and adheres to the surface of the amalgam. The plate is then covered with flannel, weights are placed upon the glass, and the stone is gently inclined so as to allow the excess of mercury to drain off; at the end of twenty-four hours it is placed upon a wooden table, the inclination of which is increased from day to day until the mirror assumes a vertical position: in about a month it is sufficiently drained to allow the mirror to be framed. The amalgam usually contains about 4 parts of tin to 1 part of mercury.

Several of the compounds of tin are employed in the arts. The dioxide is used to some extent in the preparation of enamels, and both the chlorides of tin are substances of great importance to the dyer and the calico-printer.

(925) **CHLORIDES OF TIN.**—Tin forms with chlorine two compounds, $SnCl_2$, and $SnCl_4$, formerly termed the chloride and bichloride of the metal, but now distinguished as *stannous chloride* and *stannic chloride.*

(926) **STANNOUS CHLORIDE,** formerly *Protochloride of tin,* $SnCl_2 = 189$.—The hydrate of this salt may be obtained by dissolving tin in hydrochloric acid. This solution is usually effected on the large scale in copper vessels, since the voltaic opposition of the two metals favours the solution of the tin: on evaporating the liquid until it crystallizes, prismatic needles are formed, $SnCl_2.2OH_2$ (*density* 2·710); by a heat of 100° (212° F.) it may be rendered anhydrous, but it generally loses a portion of hydrochloric acid at the same time. Stannous chloride is decomposed if mixed with a large quantity of water, hydrochloric

acid remains in solution, and a white hydrated oxychloride, $SnCl_2.SnO.2OH_2$, subsides. When exposed to the air, in crystals or in solution, stannous chloride absorbs oxygen and forms a mixture of stannic chloride and oxychloride. Stannous chloride has a strong attraction both for chlorine and for oxygen; it therefore acts as a powerful reducing agent. For example, it completely deoxidizes the salts of mercury, of silver, and of gold. Advantage is sometimes taken of this circumstance in the analytical determination of the quantity of mercury, since all the salts of mercury, when boiled with stannous chloride, are decomposed, and yield their mercury in a metallic form. Sulphurous acid is likewise deprived by it of its oxygen, producing a yellow precipitate of stannic sulphide when mixed with a solution of the salt. Stannous chloride reduces the metallic acids in the salts of chromic, tungstic, molybdic, arsenic, antimonic, and manganic acids to a lower state of oxidation; it also converts the ferric into ferrous salts, and the cupric into cuprous salts, and is a most valuable reagent in organic research for the reduction of various carbon compounds, especially nitro-derivatives. Stannous chloride is extensively employed as a mordant by the dyer and calico-printer, under the name of *salts of tin*, and they also use it for deoxidizing indigo and the peroxides of iron and manganese.* It forms double chlorides with many of the chlorides of the metals of the alkalies and alkaline earths; these double salts are crystallizable.

The anhydrous stannous chloride, or *butter of tin*, may be prepared by distilling a mixture of equal weights of tin filings and corrosive sublimate; $HgCl_2 + Sn = SnCl_2 + Hg$: it remains behind as a brilliant grey mass with a vitreous fracture; it may be distilled at a full red heat. On passing a current of chlorine over it, heat and light are evolved, and stannic chloride is formed.

(927) **STANNIC CHLORIDE**, or *Tetrachloride of tin*, formerly *Bichloride of tin*; $SnCl_4 = 260$; *Rel. wt.* 130; *Theoretic Density of vapour*, 8·996; *Observed*, 9·2; *of liquid*, 2·234 at 15° (59° F.); *Mol. Vol.* [ ]; *Boiling-pt.* 115°·3 (239°·5 F.).—This compound may be prepared either by passing dry chlorine over melted tin, or by mixing 4 parts of corrosive sublimate with 1 part of tin filings: on the application of heat a colourless liquid

* The proportion of stannous chloride available for this purpose in any commercial sample may be determined by Penny's method:—A solution of a weighed quantity of stannous chloride in hydrochloric acid is taken, and a standard solution of potassic dichromate is added until a drop of the liquid when mixed with plumbic acetate gives a yellow precipitate, showing that the chromic acid is no longer reduced: $3SnCl_2 + K_2Cr_2O_7 + 14HCl = 3SnCl_4 + 2KCl + Cr_2Cl_6 + 7OH_2$.

distils; $2HgCl_2 + Sn$ yielding $SnCl_4 + 2Hg$. It emits dense white fumes when exposed to the air, and when mixed with water, intense heat is evolved, and a hydrate ($SnCl_4.5OH_2$, Lewy) is formed which crystallizes in rhombohedra when it is allowed to form spontaneously, by exposing the chloride freely to the air; *in vacuo* it loses $3OH_2$. Although the chloride is freely soluble in a small quantity of water, copious dilution causes the precipitation of hydrated stannic acid, whilst hydrochloric acid is set free. Stannic chloride is readily soluble in water acidulated with hydrochloric acid. When its aqueous solution is mixed with a solution of the sulphate of one of the alkali-metals, hydrated stannic oxide is precipitated; $SnCl_4 + 4OH_2 + 4Na_2SO_4$ becoming $SnH_4O_4 + 4NaCl + 4NaHSO_4$, acid sulphate of the alkali-metal remaining in solution. Stannic chloride forms numerous double salts with the soluble chlorides; the compound with potassic chloride crystallizes in anhydrous octahedra, $2KCl.SnCl_4$; a similar constitution holds in the corresponding ammoniacal salt, $2NH_4Cl.SnCl_4$, which is the *pink salt* of the dyer. An impure stannic chloride is largely used by the dyers under the name of nitromuriate of tin, or *composition*; it is generally prepared by dissolving tin at a gentle heat in a mixture of nitric acid and sal ammoniac.

The *bromides* and *iodides* of tin are solid crystalline compounds closely resembling the chlorides in properties. *Stannic bromide*, $SnBr_4$, melts at 30° (86° F.) and boils at 201° (393°·8 F.).

(928) **OXIDES OF TIN.**—With oxygen, tin forms two principal compounds, the protoxide or stannous oxide, and the dioxide or stannic oxide, besides some intermediate oxides of minor importance.

(929) **STANNOUS OXIDE**, or *Protoxide of tin*, $SnO = 134$, is obtained as a white hydrate, $2SnO.OH_2$, by pouring a solution of stannous chloride into one of sodic or potassic carbonate in excess; the carbonic anhydride escapes with effervescence. When moist, this hydrate absorbs oxygen from the air, but not when dry. By ignition in closed vessels filled with nitrogen or with carbonic anhydride, it becomes anhydrous. The anhydrous protoxide may also be obtained by decomposing stannous oxalate by heat in closed vessels. If heated in the open air, it glows and is converted into the dioxide. If the hydrated protoxide be boiled with a solution of potassic hydrate in excess, it is dissolved, and in a few days metallic tin is separated, stannic oxide remaining in solution. If boiled with a weak solution of potassic hydrate, in quantity insufficient to dissolve the protoxide, it becomes anhy-

drous, and is converted into a mass of black crystalline needles; these needles when heated decrepitate powerfully, increase in bulk, and are converted into an olive-brown powder. By evaporating a solution of ammonic chloride containing hydrated stannous oxide in suspension until the ammonic chloride begins to crystallize, the oxide becomes anhydrous and assumes a brilliant scarlet colour, which, however, disappears by friction and becomes brown. Hydrated stannous oxide is readily dissolved by acids, but the anhydrous oxide is more slowly acted upon by them.

(930) **STANNIC OXIDE**, or *Binoxide of tin;* $SnO_2 = 150$; *Density*, 6·95: *Comp. in* 100 *parts*, Sn, 78·66; O, 21·34.—This oxide occurs native in the anhydrous form as *tin-stone*, and constitutes the only ore of tin that is worked. It is met with crystallized in square prisms, which are hard enough to scratch glass; they have usually a brown colour, owing to the presence of ferric oxide or of manganic dioxide, but are colourless when pure. It is insoluble in acids, but if heated with an alkali, it enters into combination with it, and forms a soluble compound.

In its hydrated condition stannic oxide has the characters of an acid, and forms two remarkable varieties which have been termed respectively metastannic and stannic acids (Fremy, *Ann. Chim. Phys.*, 1848, [3], xxiii. 393). Like the metaphosphoric and phosphoric acids, they each require a different amount of base for saturation, the stannic acid combining with the greatest proportion.

(931) **METASTANNIC ACID**, $H_2Sn_5O_{11}.4OH_2$, is readily obtained by treating metallic tin with nitric acid; a violent action takes place, attended with evolution of nitrous fumes, and the tin is converted into a white, crystalline, insoluble mass, which is hydrated metastannic acid; after washing it with cold water and drying it in the air, the acid consists of $Sn_5O_{10}.10OH_2$ (Fremy). In this state it reddens litmus-paper; when dried at 100° (212° F.) it loses half its water; at 130° (266° F.) it loses an additional molecule of water, and by ignition it becomes anhydrous, and of a pale buff colour: in this form it possesses the properties of the native dioxide, and constitutes the *putty powder* employed for polishing plate; it is also largely used for giving whiteness and opacity to enamels.

In its hydrated condition, metastannic acid is insoluble in nitric acid; concentrated sulphuric acid, when heated with it, dissolves it freely and forms a compound soluble both in water and in alcohol; by boiling, the solution is decomposed, and the two acids are separated. Hydrochloric acid combines with it,

but does not dissolve it; the compound is soluble in pure water, but is reprecipitated on the addition of acid in excess, or on boiling the solution. Metastannic acid is freely soluble in solutions of potassic and of sodic hydrates, as well as in solutions of their carbonates, but it is not dissolved by ammonia, unless recently precipitated from a cold solution of its salts by the addition of an acid; the precipitate is not soluble in ammonia after it has been boiled. The metastannates are not crystallizable, and are precipitated by adding potassic hydrate to their aqueous solution; the granular precipitate may be drained upon a tile, and dried at 130° (266° F.); their normal formula is $M'_2Sn_5O_{11}$ usually with $4OH_2$.

The potassium salt has a strongly alkaline reaction; it consists of $K_2Sn_5O_{11}.4OH_2$. The metastannates of the alkalies can only exist in the hydrated condition; if strongly heated they are decomposed, and the residue when treated with water, leaves metastannic acid, whilst the alkali is dissolved. Metastannic acid may be recognized by the beautiful golden-yellow colour which it yields when its hydrate is moistened with a solution of stannous chloride, owing to the formation of *stannous metastannate*, $Sn.Sn_5O_{11}.4OH_2$. The only metastannates which are soluble are those of potassium and sodium; they are precipitated in the gelatinous state from their solutions by the addition of almost any of the neutral salts of sodium, potassium, or ammonium.

(932) **STANNIC ACID**; $H_2SnO_3 = 168$.—This variety of the hydrated stannic oxide may be obtained by precipitating a solution of stannic chloride with ammonia, or still better by adding to the solution of the tetrachloride a quantity of an insoluble carbonate, such as chalk or baric carbonate, insufficient for its entire decomposition; it is thus separated as a gelatinous precipitate, which can be readily washed; when dried *in vacuo*, the composition of this hydrate is H_2SnO_3. It is freely soluble in hydrochloric acid, with which it reproduces stannic chloride; it is also soluble even in dilute sulphuric acid, but the stannic acid is separated on boiling: nitric acid dissolves it freely. Stannic acid is soluble in the cold in solutions of potassic and sodic hydrates, but not in ammonia; at 140° (284° F.) it is converted into metastannic acid. In combination with the alkalies it forms compounds which crystallize readily, especially from solutions which contain an excess of alkali. Their general formula is M'_2SnO_3.

The soluble stannates have a powerfully alkaline reaction; they absorb carbonic anhydride from the air when in solution, and are precipitated by solutions of most of the salts of potassium, sodium, and ammonium.

Potassic stannate, $K_2SnO_3.3OH_2$ (Moberg), is easily prepared by heating any form of stannic oxide with excess of potassic hydrate; on dissolving and

evaporating the product, transparent oblique rhombic prisms are formed. When heated to redness, potassic stannate may be rendered anhydrous. *Sodic stannate*, $Na_2SnO_3.3OH_2$, may be prepared in a manner similar to that employed for potassic stannate. It crystallizes with facility in six-sided tables, when a solution saturated at about 40° (104° F.), is heated to the boiling-point, as it is more soluble in cold than in hot water: other hydrates with 8, 9, and $10OH_2$ have been obtained. Sodic stannate is now largely prepared as a mordant for the use of the dyer and calico-printer. It forms the basis of what is technically known as *tin-prepare liquor*. Copper is quickly tinned by a solution of this salt.

Sesquioxide of Tin, or *Stannous stannate*, Sn_2O_3, or $SnO.SnO_2$, may be prepared as a slimy grey hydrate, soluble in ammonia, by boiling pure hydrated ferric oxide with a solution of stannous chloride; ferrous chloride remains in solution: $2SnCl_2 + Fe_2O_3 = 2FeCl_2 + SnO.SnO_2$. It is soluble in hydrochloric acid and also in ammonia, which latter reaction seems to indicate that it is really a distinct oxide; the hydrochloric solution gives a purple precipitate with salts of gold.

(933) The **SULPHIDES OF TIN** are three in number,—the protosulphide, the disulphide, and the sesquisulphide: the latter is unimportant.

Stannous Sulphide, or *Protosulphide of tin*, $SnS = 150$, may be procured by fusing the metal with sulphur, when it forms a bluish-grey crystalline mass, easily dissolved by melted tin; it may also be obtained by passing sulphuretted hydrogen through a stannous salt in solution, when it falls as a chocolate-brown hydrate. It is soluble in solution of ammonic disulphide, and in the sulphides of the alkali-metals if they contain an excess of sulphur. Stannous sulphide combines with the sulphides of the electronegative metals, such as arsenicum and antimony. Boiling hydrochloric acid dissolves it with evolution of sulphuretted hydrogen.

The *Sesquisulphide*, Sn_2S_3, may be prepared by mixing stannous sulphide with one-third of its weight of sulphur, and heating to dull redness; it is only partially soluble in hydrochloric acid.

Stannic Sulphide, or *Disulphide of tin*, $SnS_2 = 182$, is known as *mosaic gold*; it forms a beautiful yellow flaky compound, which is obtained by preparing an amalgam of 12 parts of tin and 6 of mercury: this is reduced to powder and mixed with 7 parts of sublimed sulphur and 6 of ammonic chloride. The mixture is introduced into a flask with a long neck, and is heated gently so long as any smell of sulphuretted hydrogen is perceptible; the temperature is then raised to low redness; calomel and cinnabar are sublimed, and a scaly mass of stannic sulphide remains. A very beautiful preparation is obtained by heating 5 parts of stannous sulphide with 8 of mercuric chloride (Woulfe). If the heat be pushed too far, part of the sulphur is expelled, and the operation fails: the ammonic chloride appears by its volatilization

to moderate the heat produced during the sulphuration of the tin, which would otherwise rise so high as to decompose the disulphide, and it mechanically preserves the requisite flaky structure of the compound. Stannic sulphide is used in the arts to imitate bronze. Aqua regia is the only acid that decomposes it, but it is readily soluble in the alkaline hydrates. A hydrated stannic sulphide, of a dingy yellow, is produced by passing sulphuretted hydrogen through a solution of one of the stannic salts. This hydrate is readily dissolved by ammonic hydric sulphide, with evolution of sulphuretted hydrogen: it is also soluble in the alkalies, and in hot hydrochloric acid. With disodic sulphide it forms a salt which may be obtained in yellow crystals, consisting of $2Na_2S.SnS_2.12OH_2$.

Stannic sulphide fuses when chlorine is passed over it; 6 molecules of the gas are absorbed, without the aid of heat, by each molecule of disulphide, and a yellow crystalline compound is obtained which may be considered as a combination of 1 molecule of stannic chloride with 2 molecules of sulphur tetrachloride; $SnCl_4.2SCl_4$.

Stannic sulphate, $Sn2SO_4$, is soluble in water strongly acidulated by sulphuric acid, but is in great part precipitated on largely diluting the solution.

(934) **Characters of the Salts of Tin.**—Tin forms two series of salts, the salts formed from the protoxide, and the salts formed from the dioxide; stannic chloride is the only salt of the latter class that has been minutely examined.

1.—The *stannous salts* or *protosalts of tin,* are nearly colourless; with the exception of the chloride, they are not often prepared: they have a powerfully astringent taste, and when in solution they absorb oxygen rapidly from the air; if largely diluted with water the solution becomes milky, but it is rendered clear by a slight excess of hydrochloric acid. The *alkaline hydrates* produce a white precipitate of hydrated stannous oxide, which is soluble in excess of the alkali, but on boiling, part of the oxide is deposited as a black crystalline powder. *Ammonia* gives a white hydrated stannous oxide, but the precipitate is not redissolved by an excess of ammonia. The *carbonates of the alkali-metals* give a similar precipitate, whilst carbonic anhydride escapes with effervescence. A very characteristic reaction is the production, with *sulphuretted hydrogen,* of a chocolate-brown precipitate of hydrated stannous sulphide. With *ammonic hydric sulphide* a similar precipitate is formed, which is soluble in excess of the precipitant and in the sulphides of the alkali-metals. With a dilute solution of *auric chloride,* they give, if used in

excess, a brown precipitate of reduced gold; in smaller quantity, they yield a beautiful purple precipitate, the purple of Cassius. *Potassic ferrocyanide* gives a white precipitate, soluble in hydrochloric acid.

2.—The *stannic salts** are found to give with the *alkaline hydrates*, a white precipitate, soluble in excess of the alkalies, and this solution yields no precipitate when boiled. *Carbonates of the alkali-metals* give a white hydrated dioxide with escape of carbonic anhydride: the precipitate is insoluble in excess of the alkaline salt. *Sulphuretted hydrogen* and *ammonic hydric sulphide* both produce a dirty yellow precipitate of hydrated stannic sulphide, which is soluble in excess of the precipitant, as well as in the sulphides of the alkali-metals, and in the alkaline hydrates.

Before the blowpipe, all the compounds of tin give white malleable globules of the reduced metal, when heated on charcoal in the reducing flame with sodic carbonate.

(935) **Estimation of Tin, and Separation from the foregoing Metals.**—Tin is estimated in the form of the anhydrous dioxide; 100 parts of which contain 78·66 of the metal.

The separation of tin from all the metals hitherto described, with the exception of cadmium, is effected by means of sulphuretted hydrogen, which precipitates none of these metals from their solutions in the mineral acids. The mixed sulphides of tin and cadmium may be at once evaporated to dryness with nitric acid: on treating the residue with water, cadmic nitrate will be dissolved, leaving an insoluble residue of metastannic acid. The cadmic sulphide is also easily separated from the sulphides of tin by ammonic disulphide, which dissolves the sulphides of tin and leaves the cadmic sulphide. Both the sulphides of tin, by ignition in a current of air, are gradually converted into stannic oxide: this change may be accelerated by moistening them with nitric acid.

Tin may also be separated from all metals with the exception of antimony (and lead if sulphuric acid be present) by evaporating the solution nearly to dryness with nitric acid, and washing the residue with water strongly acidulated with nitric acid: the tin remains as metastannic acid, and by ignition furnishes the anhydrous dioxide.

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* The presence of tartaric acid in some cases interferes with these reactions.

§ II. TITANIUM: Ti = 50. *Tetrad, as in* $TiCl_4$.

(936) **TITANIUM** is a comparatively rare metal, which presents considerable analogy with tin. It was discovered by Gregor as a constituent of *menaccanite*, in the year 1791. Its principal ores are titaniferous iron, and *rutile, anatase,* and *brookite,* which are three different forms of titanic anhydride, coloured by variable quantities of the oxides of iron, manganese, and chromium. Many clays also contain small quantities of titanic acid. When titanic anhydride is intensely heated with charcoal, it is reduced, but is not fused. A remarkable compound of the metal is frequently found, in the form of copper-coloured cubic crystals, adhering to the slags of the Welsh and other iron furnaces. These crystals, which are hard enough to scratch agate, have a density of 5·3. No acid, except a mixture of nitric and hydrofluoric acids, has any action upon them, but they are oxidized by fusion with nitre, or by ignition in a current of oxygen: they are volatile at an extremely high temperature. These crystals were supposed by Wollaston to be metallic titanium, but Wöhler showed that they consist of a combination of cyanide with nitride of titanium; they contain 18 per cent. of nitrogen, and 4 of carbon, having a formula $TiCy_2.3Ti_3N_2$. Another nitride of the metal, Ti_3N_4, also formerly mistaken for metallic titanium, although containing 28 per cent. of nitrogen, is obtained in copper-coloured scales by igniting the ammoniated titanic chloride, $4NH_3.TiCl_4$, in closed vessels, in a current of ammonia.* If a current of dry ammoniacal gas be passed over powdered titanic anhydride, heated to redness in a porcelain tube, a violet coloured titanium dinitride, TiN_2, is formed. So strong, indeed, is the attraction of titanium for nitrogen at a high temperature, that if a mixture of titanic anhydride and charcoal, both in a minute state of division, be heated to whiteness, in an atmosphere of nitrogen, the whole of the nitrogen is rapidly absorbed, whilst carbonic oxide escapes, and copper-coloured crystals, having the same composition as those obtained from the blast-furnace, are formed (Deville and Wöhler).

Titanium may be obtained by decomposing potassic fluotitanate, $2KF.TiF_4$, with potassium, in a tube filled with pure hydrogen, and through which a current of pure hydrogen is maintained. It then forms a dark green amorphous powder, which, however, contains potassium or sodium. It burns in the air with brilliant

* Ammoniated niobic chloride yields a similar nitride when treated in like manner: the same remark applies also to the corresponding molybdic compound.

scintillations and deflagrates in oxygen with dazzling brilliancy. It may be obtained in a pure state, according to S. Kern (*Chem. News*, 1876, xxxiii. 57), by passing the vapours of titanic tetrachloride over fused sodium. The product is washed with water and dried over sulphuric acid. Deville also obtained metallic titanium in square prisms by decomposing the vapour of the tetrachloride with sodium. Chlorine at ordinary temperature does not kindle titanium, but if heated, the metal burns in the gas with almost as much splendour as in oxygen. Titanium is soluble in hydrochloric acid with evolution of hydrogen, forming a colourless solution, from which ammonia precipitates a black hydrated protoxide.

(937) **TITANOUS CHLORIDE,** $Ti_2Cl_6 = 313$, is prepared by heating titanic chloride in an atmosphere of hydrogen; it forms dark violet scales. It is also formed on heating the tetrachloride with metallic silver at 200° (392° F.): as it is not volatile without decomposition, however, it must be extracted by means of water from the product; on evaporating, a hydrate of the composition, $Ti_2Cl_6\,8OH_2$, is obtained. The same hydrate is produced on dissolving titanium in hydrochloric acid. When titanous chloride, Ti_2Cl_6, is heated in a current of hydrogen above 440° (824° F.) titanic chloride, $TiCl_4$, distils over, and a *dichloride of titanium*, $TiCl_2$, is left. This new chloride must be cooled in a current of carbonic anhydride, as it absorbs hydrogen, and air causes it to take fire. It has a very strong attraction for water, and at the same time undergoes decomposition (Friedel, *Compt. Rend.*, 1875, lxxxi. 889).

(938) **TITANIC CHLORIDE,** or *Tetrachloride of titanium*, $TiCl_4 = 192$; *Rel. wt.* 96; *Theoretic Density of vapour*, 6·643; *Observed*, 6·836; *of liquid*, 1·761 *at* 0° (32° F.); *Mol. Vol.* [ ]; *Boiling-pt.* 135° (275° F.).—This is a fuming volatile liquid, resembling stannic chloride. It may be obtained by decomposing pure titanic anhydride, intimately mixed with charcoal, and heated to redness in a porcelain tube, by means of a current of dry chlorine gas. It is a colourless liquid, which combines with a small quantity of water to form a crystallizable compound, which, according to Merz, is an oxychloride. A large quantity of water occasions its decomposition, hydrated titanic acid being separated. An *oxychloride of titanium* of the formula, $Ti_2O_2Cl_2$, has been obtained in brownish-red crystals, and another, $Ti_4Cl_2O_6$, by the direct action of oxygen on the tetrachloride.

(939) **TITANIC FLUORIDE,** $TiF_4 = 126$, is a fuming colourless liquid obtained on distilling a mixture of fluor-spar and titanic anhydride with sulphuric acid in a platinum retort. Water decomposes it, producing insoluble titanic oxyfluoride and soluble hydric titanic fluoride or fluotitanic acid, $2HF.TiF_4$, analogous to hydrofluosilicic acid, $2HF.SiF_4$. A *titanous fluoride*, Ti_2F_6, is formed on igniting potassic fluotitanate in a current of hydrogen, and is left as a violet powder on treating the product with hot water.

(940) **OXIDES OF TITANIUM.**—Three of these probably exist—the protoxide, the sesquioxide, and the dioxide, or titanic anhydride.

The *protoxide*, $TiO = 66$, has not been obtained in a pure state. It appears to be formed when titanic anhydride is heated in a crucible lined with charcoal: but where the anhydride is actually in contact with the charcoal, a film of metallic titanium, mixed with a portion of nitride, is obtained. The protoxide is a black powder nearly insoluble in acids, and is gradually oxidized by exposure to a high temperature in the air, or by fusion with nitre; the same oxide appears to be precipitated as a dark purple powder when a solution of titanic acid in hydrochloric acid is digested with zinc.

If a solution of titanic acid in hydrochloric acid be digested with metallic copper at 50° (122° F.), and the resulting violet blue solution be poured into ammonia, a dark brown hydrated *sesquioxide*, $Ti_2O_3.xOH_2$, or titanous titanate, $TiO.TiO_2$, is deposited, which absorbs oxygen from the air with great rapidity, and becomes white from the formation of titanic acid. Hydrochloric acid dissolves it sparingly, and forms a blue solution. The anhydrous compound, Ti_2O_3, has also been obtained in minute red crystals along with the oxychloride, $Ti_2O_2Cl_2$, as a product of the reaction of hydrogen and titanic chloride on titanic acid. A *sulphate of the sesquioxide* of the formula, $Ti_2(SO_4)_3.8OH_2$, may be obtained in crystals by dissolving the metal in dilute sulphuric acid and evaporating.

TITANIC ANHYDRIDE, or *Titanic dioxide;* $TiO_2=82$.—This compound occurs in *menaccanite* and *iserine* as ferrous titanate; but more commonly it is met with in the uncombined condition, constituting the principal ore of the metal. It is found native under three distinct crystalline forms, each of which has a different density. Of these, the densest and most abundant is *rutile* (density 4·25), which occurs in long striated prisms or needles of a brown colour, isomorphous with those of tin-stone. The second variety, *brookite* (density 4·13), is found in right rhombic prisms, sometimes opaque, at others transparent, and of a pale brown colour; whilst the third variety, *anatase* (density 3·9), is found in Dauphiné, in acute octahedra which are semi-transparent, and of a yellowish-brown or blue colour. Corresponding differences are observed in the titanic dioxide artificially prepared in the laboratory. Ebelmen obtained needle-shaped, transparent, yellow crystals of rutile of density 4·283 by prolonged heating in a porcelain kiln, of a mixture of 1 part of powdered titanic dioxide and 5 parts microcosmic salt. Like stannic oxide, it may, when hydrated, be obtained in two isomeric forms possessed of different properties. In fact, the existence of two dissimilar modifications is a very usual occurrence in the case of metallic oxides possessed of feeble acid powers.

Pure titanic dioxide may be obtained by reducing rutile, or titanic iron-sand to a fine powder, and fusing it with thrice its weight of potassic carbonate. On treating the mass with hot water, an impure hydric potassic titanate remains; this is dissolved in hydrochloric acid, precipitated by an excess of ammonia, and the precipitate digested in ammonic hydric sulphide, by which the tin, iron, and manganese are converted into sulphides, whilst the titanic acid remains unchanged; the sulphides can then be dissolved out by a solution of sulphurous acid, leaving a pure white hydrated titanic acid. The water may be expelled by heat, and by long-continued ignition the colour of the compound deepens, and its specific gravity increases until it acquires a density equal to that of rutile. In this state it is insoluble

either in solutions of the alkalies, or in acids, except hydrofluoric acid and boiling oil of vitriol. This anhydride may, however, be brought into solution by heating it with a fixed alkaline carbonate, and dissolving the residue in cold hydrochloric acid; the titanic acid can be precipitated from the solution by means of ammonic sesquicarbonate: it then forms a white gelatinous hydrate, which dries into a semi-transparent mass capable of reddening litmus. The liquid long remains turbid; it cannot be rendered clear by filtration, unless an excess of some ammoniacal salt be present. Hydrated titanic acid is insoluble in solutions of the alkaline hydrates, but it yields definite salts with them. When fused with potassic hydrate, it forms a transparent yellowish glass. The hydrated titanic acid is soluble in dilute hydrochloric acid, and also in concentrated sulphuric acid, forming a definite sulphate, $TiO_2.SO_3$, which may be evaporated to dryness at a low temperature without undergoing decomposition: this is a basic sulphate, but the normal sulphate, $Ti(SO_4)_2.3OH_2$, may be obtained by oxidizing the sulphate of the sesquioxide, $Ti_2(SO_4)_3.8OH_2$, with nitric acid; it forms a yellowish, amorphous, transparent mass. Both these acid solutions when diluted and boiled for a long time are decomposed, and the insoluble variety of titanic acid is precipitated. When the soluble hydrate is heated, it loses water and becomes converted into the anhydride. This compound becomes yellow on ignition, but recovers its whiteness on cooling. Titanic anhydride is dissolved by fused hydric potassic sulphate, the product being soluble in water; it may thus be distinguished and separated from silica, which is not rendered soluble by this means.

The hydrated titanic acids are very numerous, and their composition is as yet far from being definitely settled.

(941) **TITANIC SULPHIDE,** TiS_2, may be obtained in large yellow scales with a metallic lustre by passing the vapour of carbonic bisulphide over strongly ignited titanic anhydride; it is not soluble in the sulphides of the alkali-metals, and when ignited in the air it burns readily, forming titanic anhydride and sulphurous anhydride.

(942) **Characters of the Compounds of Titanium.**—1.—The *titanous salts* are but little known: with the *carbonates of the alkali-metals* they give a blue precipitate, which becomes first brown and ultimately green.

2.—The *titanates* of the alkali-metals are of a yellowish-white colour: the normal salts are insoluble in cold water; hot water removes the alkali, while most of the titanic acid remains undissolved. Cold hydrochloric acid dissolves them, forming a solu-

tion which, when boiled, becomes turbid from deposition of titanic acid: *ammonia*, when added to this solution, produces a white precipitate. *Ammonic phosphate* gives a gelatinous precipitate when added to a hydrochloric solution of titanic acid. *Infusion of galls* produces an orange-coloured precipitate in the acid solution of the titanates; a precipitate of a similar colour is produced by *potassic ferrocyanide*. In the reducing flame of *the blowpipe* the titanates give with microcosmic salt a beautiful purple or bluish glass, which becomes colourless in the oxidizing flame. This reaction distinguishes the titanates from the tantalates.

(943) **Estimation of Titanium.**—Titanium is always estimated in the form of titanic anhydride. Its solution in cold hydrochloric acid is not precipitated by sulphuretted hydrogen, a circumstance which may be taken advantage of in separating it from tin and cadmium, both of which are thrown down from the acid as insoluble sulphides. The solution is next mixed with tartaric acid, and supersaturated with ammonic hydric sulphide: iron, nickel, cobalt, manganese, and zinc are thus separated in the form of sulphides. The solution is afterwards evaporated to dryness, and the tartaric acid is burned off; titanic anhydride is left, mixed with the salts of the earths and alkalies contained in the mixture; the residue is fused with potassic hydrate, redissolved in the cold by hydrochloric acid, and on boiling the liquid, to which a little dilute sulphuric acid has been added, the titanic acid is precipitated, collected, and converted into the anhydrous dioxide by ignition. This process, however, does not yield very accurate results; indeed the exact determination of the quantity of titanium in its compounds is a matter of considerable difficulty.

§ III. ZIRCONIUM AND THORINUM.

(944) **ZIRCONIUM**, $Zr^{iv} = 89{\cdot}5$, is the elementary base of an oxide contained in the *zircon* and the *hyacinth*, which are zirconic silicates of similar composition, $ZrO_2.SiO_2$. The metal is obtained on heating the potassic fluozirconate, $2KF.ZrF_4$, with potassium, and treating the residue when cold with dilute hydrochloric acid, by which everything except the zirconium is dissolved: it is thus left in a pulverulent form, and must be washed, first with a solution of ammonic chloride, and then with alcohol; if water be used for the washing, the finely divided zirconium passes through the filter in suspension in the water. As thus obtained it is in the form of a black amorphous powder, which does not conduct a feeble voltaic current: under the burnisher it assumes a slightly metallic lustre: in the air or in oxygen, it takes fire below a red heat and burns brilliantly, forming zirconia of snowy whiteness: dilute sulphuric and hydrochloric acids do not act on it. Hydrofluoric acid dissolves it with evolution of hydrogen, forming a fluoride closely resembling fluotitanic acid: it yields a number of fluozirconates with the fluorides of the basylous metals, which have the general formula, $2MF.ZrF_4$. Boiling water gradually oxidizes amorphous zirconium; if heated with sulphur *in vacuo* it forms a brown pulverulent *disulphide*, which is not decomposed by sulphuric or hydrochloric acid, and is but slowly attacked by aqua regia. According to Troost (*Compt. Rend.*, 1865, lxi. 109), zirconium may also be obtained in crystalline plates of density 4·15; it is less fusible than silicon. This crystallized zirconium may be prepared by heating 1 part of potassic fluozirconate, $2KF.ZrF_4$, with $1\frac{1}{2}$ aluminium in a crucible of gas-coke,

to the fusing-point of iron: plates of zirconium are sometimes formed a centimetre broad, and may be freed from aluminium by digestion in hydrochloric acid diluted with twice its volume of water. The zirconium is mixed with plates of an alloy of aluminium and zirconium, the proportions of which are variable. In this form it may be heated in the air without taking fire, but burns in the oxyhydrogen flame. Fused potassic hydrate oxidizes the crystals with evolution of hydrogen. Melted nitre and potassic chlorate do not act upon it. Concentrated nitric and sulphuric acid act on zirconium very slowly, and only when heated with it; hot hydrochloric acid also attacks it very slowly. Aqua regia when heated acts rapidly on it; but hydrofluoric acid, whether strong or dilute, dissolves it readily, even in the cold. Zirconium has also been obtained in the graphitoïdal modification by heating sodic zirconate with iron: it forms light scales of a steel-grey colour. Zirconium is intermediate in properties between silicon and titanium, to which latter body it is more allied than to any other element, as is particularly seen in the properties of the zirconic tetrafluoride, and of the fluozirconates.

(945) **ZIRCONIC CHLORIDE** ($ZrCl_4 = 231{\cdot}5$; *Mol. Vol.* [□]; *Rel. wt.* 115·75; *Theoretic Density of Vapour*, 8·006; *Observed*, 8·15), crystallizes in needles which are soluble in water and in alcohol; they effloresce in the air, and lose water and hydrochloric acid, leaving a soluble oxychloride.

(946) **ZIRCONIC FLUORIDE**, ZF_4.—Zirconic hydrate dissolves easily in hydrofluoric acid, ignited zirconia with difficulty, and the solution when evaporated leaves hydrated zirconic fluoride, $ZF_4.3OH_2$, in small crystals belonging to the triclinic system. The anhydrous fluoride may be obtained by igniting pure zirconia with twice its weight of ammonic hydric fluoride.

(947) **ZIRCONIA**; $ZrO_2 = 121{\cdot}5$; *Density*, 4·3 to 4·9.—Zirconium forms but one oxide, which Berzelius regarded as the sesquioxide, although most chemists now adopt the view of Dumas and of De Marignac, who consider it to be a dioxide, like silica. It may be obtained by fusing very finely powdered zircon with potassic or sodic hydrate, and saturating with hydrochloric acid. The excess of acid and moisture is expelled by evaporating nearly to dryness; on the addition of water, the zirconic chloride is dissolved, leaving the silica; the solution, which usually contains ferric oxide, is then boiled with sodic thiosulphate (hyposulphite of soda); this precipitates the zirconia as thiosulphate, leaving the iron in solution; on igniting the thiosulphate, pure zirconia is left. Zirconia forms a white infusible powder, which, after ignition, is insoluble in all acids, except hydrofluoric or strong sulphuric acid. The hydrate, ZrH_2O_3, is a gelatinous, bulky, white precipitate, very sparingly soluble in ammonic sesquicarbonate. It is insoluble in the alkaline hydrates. If the salts of zirconium be precipitated by an alkaline carbonate, the precipitate becomes redissolved on agitation with excess of the carbonate; a bicarbonate takes up still more, and by boiling the solution, a portion of the zirconia is deposited. Zirconia when fused with the carbonates of the alkali-metals decomposes them, carbonic anhydride being evolved, and a compound of zirconia with the alkali being formed. If a neutral solution of zirconic sulphate to which potassic sulphate has been added be boiled, a characteristic decomposition occurs, and a basic sulphate of zirconium falls, whilst hydric potassic sulphate is formed and remains dissolved.

Zirconia is distinguished from alumina and glucina by its insolubility in the *alkaline hydrates*. Its salts have a purely astringent taste; when their neutral solutions are boiled with one of *potassic sulphate*, a sparingly soluble subsulphate of the earth is formed. *Tincture of galls* gives a yellow precipitate in their solutions; *potassic ferrocyanide* does not precipitate them.

(948) **THORINUM**, Th = 234, was discovered in 1829, by Berzelius, in a rare black mineral termed *thorite*, found in a syenitic rock in Norway. It has also been found in euxenite, pyrochlore, and a few other rare minerals. This metal, like aluminium, is prepared from its chloride, which is a volatile compound obtained by heating an intimate mixture of thorina and finely divided charcoal in a current of dry chlorine. Thorinum is a grey metallic powder of density 7·6 to 7·8, closely resembling zirconium, it takes fire, however, considerably below a red heat, and burns with great brilliancy; the resulting oxide shows no traces of fusion. *Thorinic chloride*, $ThCl_4$, is prepared by passing dry chlorine over a heated mixture of thorina and charcoal. It crystallizes in rectangular four-sided tables, $ThCl_4.8OH_2$, which are deliquescent, and very soluble in water. *Thorina* appears to be a dioxide, ThO_2, and is remarkable for its high density, 9·402. It is insoluble in solutions of the alkaline hydrates, but is dissolved without difficulty in those of their carbonates. After it has been ignited it is no longer soluble in any acid except concentrated sulphuric. The hydrate has the formula, ThH_4O_4. Its salts have an astringent taste, and their solutions give a white precipitate with potassic ferrocyanide. *Thorinic sulphate*, $Th2SO_4$, with potassic sulphate, forms *thorinic potassic sulphate*, $ThK_44(SO_4).2OH_2$, which is soluble in water, but is precipitated by a saturated solution of potassic sulphate. Thorinic sulphate exhibits the characteristic peculiarity of being precipitated on boiling its solution, but it is slowly redissolved on cooling: its crystals, like those of yttric sulphate, when heated become milk-white without any alteration of form: oxalic acid gives, with salts of thorinum, even in acid solutions, a white insoluble oxalate of the metal.

§ IV. MOLYBDENUM: Mo = 96.

(949) **MOLYBDENUM**; *Density*, from 8·615 to 8·636; *Dyad, Tetrad, and Hexad, as in* $Mo''Cl_2$; $Mo^{iv}Cl_4$: $Mo^{vi}O_3$.—The principal ore of molybdenum is the disulphide, a mineral which occurs chiefly in Bohemia and in Sweden, in appearance much resembling plumbago, hence its name, from *μολύβδαινα*, 'a piece of lead.' Molybdenum is also occasionally found as an oxide, in combination with lead, as plumbic molybdate. The metal may be obtained from the pure native sulphide; on roasting it at a gentle heat in a free current of air, the sulphur passes off as sulphurous anhydride, whilst the molybdenum also combines with oxygen, and remains behind in the form of molybdic anhydride. If this be mixed into a paste with oil and charcoal, and exposed to the heat of a smith's forge, in a crucible lined with charcoal, it is reduced to the metallic state, or the oxide may be heated to whiteness in a porcelain crucible with potassic cyanide. In this form molybdenum is white, brittle, and very difficult of fusion. The anhydride may also be reduced by heating it to redness in a porcelain tube in a current of hydrogen; when the pulverulent metal thus obtained is heated in the open air it is gradually oxidized, and finally converted into molybdic anhydride. It is readily oxidized by nitric acid; if the metal be in excess, a

soluble nitrate of the dioxide is obtained, but if the acid predominate, the oxidation proceeds further, and molybdic acid is formed: aqua regia produces similar results. Molybdenum is also oxidized when fused with nitre, potassic molybdate being produced.

(950) **CHLORIDES OF MOLYBDENUM.**—There are four chlorides of molybdenum known, as follows:

Molybdic pentachloride	$MoCl_5$
Molybdic tetrachloride	$MoCl_4$
Molybdic trichloride	Mo_2Cl_6
Molybdic dichloride	$MoCl_2$

Molybdic Pentachloride, $MoCl_5 = 273{\cdot}5$.—This compound is formed by the action of chlorine on molybdenum: to prepare it, the metal should be first heated in dry hydrochloric acid until there is no further action, and allowed to cool in a current of the gas; the hydrochloric acid is then replaced by a current of dry chlorine free from oxygen, and the metal gently heated until it is entirely converted into the black pentachloride. It forms a crystalline mass, which melts and volatilizes without decomposition, yielding a dark brown red vapour. It is, however, very readily acted on both by oxygen and by moisture. According to Debray it melts at 194° (381·2 F.), and boils at 268° (514°·4 F.).

Molybdic Trichloride, $Mo_2Cl_6 = 405$.—The trichloride is produced when the pentachloride is heated in a current of hydrogen at 250° (482° F.). It is an amorphous red compound which is insoluble in water and permanent in the air, having an appearance closely resembling that of 'amorphous phosphorus.'

When the trichloride is heated to redness in a current of carbonic anhydride free from oxygen, it is resolved into the *dichloride*, $MoCl_2$, and the *tetrachloride*, $MoCl_4$, according to the equation; $Mo_2Cl_6 = MoCl_2 + MoCl_4$. The dichloride is an amorphous substance of a brilliant yellow colour, which is not volatile at a red heat. It is permanent in the air at ordinary temperatures, and insoluble in water and in dilute nitric acid. It dissolves readily, however, in hot hydrochloric acid, and on cooling, the hydrate, $Mo_2Cl_4.3OH_2$, separates in long yellow lustrous needles. When the trichloride is heated in a current of carbonic anhydride, the tetrachloride sublimes as a brown, indistinctly crystalline mass, which is easily decomposed by water or by the action of oxygen.

(951) **Bromides of Molybdenum** have also been prepared. The compound, $MoBr_2$, is easily obtained as a yellowish-red mass on heating metallic molybdenum in bromine vapour.

(952) **OXIDES OF MOLYBDENUM.**—Molybdenum forms three oxides; the protoxide, MoO?, and the dioxide, MoO_2, are both possessed of basic characters: the third, molybdic anhydride, MoO_3, reacts energetically with bases, and yields well characterized salts. Besides these there are several oxides intermediate between Mo_2 and Mo_3, which may be regarded as molybdic molybdates.

The *protoxide*, ?MoO = 112, is precipitated, by excess of ammonia, from the solution of a molybdate in hydrochloric acid which has been reduced by means of a bar of zinc; it is thus thrown down as a black hydrate which absorbs oxygen from the air: it is soluble in a solution of ammonic sesquicarbonate, but not in those of the fixed alkalies or their carbonates. It may also be obtained in the anhydrous form, by digesting molybdic anhydride with zinc and hydrochloric

acid. According to Rammelsberg this oxide is a sesquioxide, and he doubts the existence of a protoxide.

The *dioxide*, $MoO_2 = 128$, may be obtained in dark violet-coloured prisms by fusing sodic molybdate with one-third its weight of zinc, and treating the product alternately with potassic hydrate and hydrochloric acid. The crystals, which have a metallic lustre, are reddish-violet by transmitted light. They are converted into the trioxide by boiling with nitric acid. It may also be prepared by igniting a mixture of sodic molybdate with sal ammoniac, and treating the mass with a solution of potassic hydrate. The hydrated dioxide may be prepared by digesting molybdic anhydride mixed with copper filings, in hydrochloric acid; an excess of ammonia precipitates the dioxide of a rusty brown colour, whilst the copper is retained in solution. Hydrated molybdic dioxide is soluble in pure water, but is precipitated by the addition of any salt. The solution gelatinizes on keeping. The salts which this oxide forms with acids are of a reddish-brown colour, or, if anhydrous, are nearly black.

If a solution of molybdic tetrachloride, $MoCl_4$, be added, drop by drop, to a concentrated solution of the acid-molybdate of ammonium, a deep blue precipitate of *molybdic tetramolybdate*, $MoO_2.4MoO_3$, is formed. This compound is soluble in water, but is precipitated by the addition of any saline body. The addition of a small quantity of a stannous salt to a soluble molybdate reduces the molybdic acid, and produces this beautiful blue compound, which may serve as a test of the presence of molybdic acid: care must be taken not to add the tin salt in excess. The *molybdic dimolybdate*, $MoO_2.2MoO_3$, has a green colour.

(953) **MOLYBDIC ANHYDRIDE**, or *Molybdic trioxide*; $MoO_3 = 144$; *Density*, 3·49; *Comp. in* 100 *parts*, Mo, 66·67; O, 33·33.—This compound is obtained in an impure form, by roasting the native molybdic disulphide at a low red heat; it remains behind as a dirty yellow powder; caustic ammonia dissolves the trioxide, leaving ferric oxide and other impurities. The ammoniacal solution crystallizes on evaporation, and at a low red heat ammonia is expelled, leaving the trioxide behind, of a pale buff colour. The trioxide reddens moistened litmus-paper, and is sparingly soluble in water, forming a yellow solution. At a red heat it fuses to a straw-coloured glass of density 3·49 which undergoes volatilization in open vessels, and is deposited on cool surfaces in brilliant transparent needles: on heating native molybdic sulphide in a porcelain tube in a gentle current of air, beautiful crystals of the anhydride are deposited in the cool part of the tube. No definite hydrated molybdic acid is known. When precipitated from its salts by the addition of an acid, it may be redissolved, if the acid be added in excess: it forms a compound with sulphuric acid, which may be obtained in colourless, brilliant crystals of the formula, $M_2O_2.SO_4$, on evaporating a solution of molybdic anhydride in moderately concentrated sulphuric acid. It is also freely soluble in a solution of hydric potassic tartrate (cream of tartar).

Molybdic acid forms well characterized salts, both normal and acid. Those

of the alkalies are soluble. Normal or *diammonic molybdate* crystallizes in colourless square prisms. An *acid ammonic molybdate*, NH_4HMo_4, crystallizes readily in six-sided prisms: when sodic molybdate is boiled with ammonic chloride, an ammonic molybdate, containing a large excess of acid, is slowly precipitated. Various anhydro-molybdates of the alkalies have been formed, which contain as many as 3, 4, 8, 10, and even 16 molecules of the anhydride to 1 of fixed base. According to Delafontaine the soluble acid molybdates have a general formula, $3M'_2O.7MoO_3$. *Plumbic molybdate*, $PbMoO_4$, occurs native in crystals of a yellow colour; it is soluble in nitric acid, and in solution of potassic hydrate if the alkali be in large excess.

A solution of ammonic molybdate may be advantageously employed in certain cases to detect the presence of very small quantities of phosphoric acid in solution. The solution suspected to contain the phosphate must be acidulated with nitric acid, and the molybdate then added. The liquid becomes yellow, and on boiling, deposits a yellow crystalline precipitate, consisting of molybdic and phosphoric acids in combination with ammonia. According to Sonnenschein, it contains 6·747 per cent. of ammonia, and about 3 per cent. of P_2O_5. Arsenic acid forms a similar compound with ammonic molybdate when the solutions are boiled (comp. Debray, *Compt. Rend.*, 1874, lxxviii. 1408).

Sonnenschein takes advantage of the insolubility of the phosphoric compound to detect small quantities of ammonia by its means. In order to prepare the test solution, he first prepares the yellow precipitate, by adding ammonic molybdate to an acidulated solution of hydric disodic phosphate, ignites the precipitate to expel the ammonia, adds nitric acid to the residue, in order completely to reoxidize any reduced molybdic acid, evaporates to dryness, and expels the nitric acid by ignition. A solution of sodic carbonate is employed to dissolve the remaining mixture of phosphoric and molybdic acids, and the solution is supersaturated with hydrochloric acid. This liquid, it is stated, will easily detect the presence of 1 part of ammonic chloride in 10,000 of water. Sodic salts are not affected by it, but strong solutions of the potassic salts yield a similar yellow precipitate.

(954) **MOLYBDENUM OXYCHLORIDES.**—A *chloromolybdic acid* or *molybdic dioxydichloride* sublimes in yellowish scales when the dioxide is heated in a current of chlorine. It is soluble both in water and in alcohol, and consists of $MoCl_6.2MoO_3$, or MoO_2Cl_2. The same compound is formed on heating the pentachloride or tetrachloride of molybdenum in a current of chlorine: other oxychlorides exist. Compounds somewhat similar may be formed with many acidifiable metals, such, for example, as tungsten, chromium, and vanadium.

(955) **SULPHIDES OF MOLYBDENUM.**—Three sulphides of molybdenum are known, MoS_2, MoS_3, and MoS_4: the last two are sulphur anhydrides.

Molybdic Disulphide, or *Bisulphide of molybdenum;* MoS_2= 160; *Density*, 4·6; *Comp. in* 100 *parts*, Mo, 60; S, 40.—This sulphide is the principal ore of the metal: it is a soft solid of a leaden-grey colour and metallic lustre. The disulphide may also be formed artificially by heating molybdic anhydride in the vapour of sulphur. It is unchanged by heat in closed vessels, but if roasted in the open air, sulphurous anhydride is formed and volatilized, whilst molybdic anhydride remains. Nitric acid decomposes it, and converts the metal into molybdic acid; sulphuric acid also decomposes it when boiled with it, forming a blue solution, whilst sulphurous anhydride escapes.

Molybdic Trisulphide, MoS_3 = 192.—This is precipitated on passing sulphuretted hydrogen through a solution of a molybdate, and adding hydrochloric acid. It is of a dark-brown colour, and forms sulphur salts with the sulphides of the alkali-metals. The potassium salt, K_2MoS_4, crystallizes in magnificent iridescent crystals. The *molybdic tetrasulphide* also combines readily with the sulphides of the alkali-metals.

(956) **Characters of the Salts of Molybdenum.**—1.—Little is known of the *molybdous salts*, or salts corresponding to the protoxide. They yield a dark-brown precipitate with the *hydrates of the alkalies* and their *carbonates;* the precipitate is soluble in excess of ammonic sesquicarbonate, and is deposited again on boiling the liquid; *sulphuretted hydrogen* slowly produces a brown precipitate of hydrated sulphide, which is soluble in ammonic hydric sulphide.

2.—The salts corresponding to the *dioxide* have a dark colour, and a metallic astringent taste. *Infusion of galls* produces with them a brownish-yellow solution; *potassic ferrocyanide* gives a dark-brown precipitate; *ammonia* a rusty-brown precipitate of the hydrated dioxide.

3.—The *molybdates* yield characteristic reactions with zinc, tin, and copper. With *zinc* in dilute acid solutions, the liquid becomes first blue, then green, and finally black, after which the addition of ammonia produces a deposit of hydrated molybdous oxide. The addition of a small quantity of *stannous chloride* in solution to a liquid containing a molybdate, produces the beautiful blue molybdic tetramolybdate, $MoO_2.4MoO_3$, previously mentioned, but care must be taken not to have the tin salt in excess, or the precipitate becomes of a dull green. *Copper filings* in similar solutions reduce the molybdic acid to the dioxide, which is precipitated as a brown hydrate by ammonia. *Before the blowpipe*, the compounds of molybdenum yield, in the oxidizing flame, a colourless bead with borax, and with microcosmic salt; in the reducing flame they give a brownish-red bead with borax, and a green one with microcosmic salt.

Molybdenum is usually estimated in the form of the disulphide, of which 100 parts contain 60 of the metal.

§ V. TUNGSTEN: (Wolframium) W = 184.

(957) **TUNGSTEN**; *Density, 17·6; Tetrad and Hexad, as in* WCl_4 and WCl_6.—This metal is found in small quantities in the mineral known as *Scheelite* or calcic tungstate, $CaWO_4$, and also in *wolfram*, as a ferrous manganous tungstate, $MnWO_4.3FeWO_4$. It is easily obtained from the calcic tungstate by digesting the powdered mineral in hydrochloric acid, which combines with and dissolves the calcium, but leaves the insoluble tungstic acid behind: the metal itself is prepared from this compound by heating it to bright redness in a current of hydrogen gas; as thus obtained it is of a dark-grey colour, but assumes a metallic lustre under the burnisher. If tungstic anhydride be made into a paste with oil, and heated intensely in a crucible lined with charcoal, for some hours, tungsten is obtained as a heavy iron-grey metal, which is very hard, and difficult of fusion. It may be heated in the air whilst in the compact state without sensible change, but in the pulverulent form it burns easily into tungstic anhydride. Aqua regia and nitric acid convert it into tungstic acid, and the same change is produced by heating it in contact with the alkalies or with nitre. Pulverulent tungsten is also oxidized and dissolved by boiling it in a solution of the alkaline hydrates or carbonates. When tungsten is alloyed in the proportion of 9 or 10 parts with 90 of steel, it yields a metallic mass of extraordinary hardness.

(958) **CHLORIDES OF TUNGSTEN.**—Four chlorides of this metal are known, of which two, the hexachloride and the pentachloride, are volatile without decomposition:

Tungstic hexachloride	WCl_6
Tungstic pentachloride	WCl_5
Tungstic tetrachloride	WCl_4
Tungstic dichloride	WCl_2

TUNGSTIC HEXACHLORIDE, WCl_6, (*Theoretic Density of Vapour, 13·805; Observed, 11·86*; Debray), is formed by passing pure and dry chlorine over heated metallic tungsten; also by the action of phosphoric pentachloride on tungstic anhydride: $WO_3 + 3PCl_5 = WCl_6 + 3POCl_3$. When pure it fuses at 275° (527° F.), and boils at 347° (656°·6 F.), but the presence of mere traces of oxychloride greatly lowers the melting point. The pure hexachloride forms a black violet crystalline sublimate, and is neither altered by exposure to moist air nor acted on by water at temperatures below 60° (140° F.): when traces of oxychloride are present, however, it is of a bronze colour, and by exposure to the air it absorbs moisture and quickly acquires a violet hue; it is also readily soluble in cold water, being, at the same time, decomposed.

Tungstic Pentachloride, WCl_5, is formed together with the tetrachloride on heating the hexachloride in a current of hydrogen at a low temperature; the volatile pentachloride may then be separated by distillation. It forms black, lustrous, deliquescent needles which melt at 248° (478·4 F.), and boil at 275° (527° F.).

Tungstic Tetrachloride, WCl_4, forms the non-volatile residue in the preparation of the pentachloride, provided the temperature has not been too high. It is a soft crystalline hygroscopic powder which, when strongly heated, splits up into the pentachloride which volatilizes, and the *dichloride* which remains behind.

Tungstic tetrachloride, WCl_4, absorbs ammonia, and by a gentle heat, the whole of the chlorine is expelled in the form of sal ammoniac, leaving a black powder consisting of $2WN_2.WH_4N_2$. When this powder is heated in the air it burns, evolving ammonia and leaving a residue of tungstic anhydride.

Tungstic dichloride, WCl_2, is a greyish powder which yields the brown oxide, WO_2, when treated with water (Roscoe, *Jour. Chem. Soc.*, 1872, xxv. 287).

(959) **BROMIDES OF TUNGSTEN.**—Bromine compounds of tungsten, corresponding to the penta- and dichlorides, have been obtained. The *pentabromide*, WBr_5, forms dark coloured crystals resembling iodine in appearance. Heated at 330° (626° F.), in hydrogen, it yields the *dibromide*, WBr_2.

The only compound of iodine and tungsten known is the *diiodide*, WI_2, which is formed when the vapour of iodine is passed over the heated metal.

(960) **OXIDES OF TUNGSTEN.**—Two of these are known, viz., a dioxide, WO_2, which does not form salts with acids, and an acid trioxide, WO_3. Wöhler attributes to an intermediate oxide the composition of *tungstous tungstate*, $WO_2.WO_3$: it is of a splendid blue colour, somewhat analogous to the molybdic molybdates, and may be obtained by a partial reduction of tungstic acid, either by hydrogen gas, or by strongly igniting ammonic tungstate in closed vessels, or by digesting tungstic anhydride with zinc and hydrochloric or sulphuric acid.

(961) **TUNGSTIC DIOXIDE,** or *Tungstous oxide*, WO_2.—It is obtained as a brown powder by heating tungstic trioxide to low redness in a stream of hydrogen; or in copper-coloured scales, by adding tungstic anhydride to dilute hydrochloric acid in which some pieces of zinc have been placed. In the latter form it attracts oxygen rapidly from the air, and is dissolved by a solution of potassic hydrate, with evolution of hydrogen and formation of potassic tungstate. Wöhler obtains the dioxides from wolfram by fusing 3 parts of this mineral with 6 parts of potassic carbonate: the melted mass is treated with boiling water, filtered, and mixed with a solution of 4 parts of ammonic chloride. The solution is then evaporated to dryness, and the residue ignited; upon treating the mass with boiling water, the dioxide remains as a heavy black powder, which must be washed, first with a weak solution of potassic hydrate, and afterwards with water. In this operation the hydrogen of the ammoniacal salt partially reduces the tungstic acid of the mineral.

With soda, tungstic oxide forms a remarkable compound of a yellow colour, and metallic lustre, containing, according to Wright, $Na_2O.WO_2.WO_3$. It crystallizes in cubes, and is not acted upon by any acid, or mixture of acids, except the hydrofluoric; solutions of alkaline hydrates are equally without effect upon it: if heated in the air it is decomposed and partially converted into

sodic tungstate. It is best obtained by fusing tin with an excess of the acid sodic tungstate: in order to remove the undecomposed sodic tungstate and free tungstic acid, the residue is treated in succession with concentrated solution of potassic hydrate, water, and hydrochloric acid; finally it is washed with water. Corresponding compounds with potassium and lithium have also been obtained.

(962) **TUNGSTIC ANHYDRIDE**, or *Trioxide*; $WO_3 = 232$; often called *tungstic acid; Density*, 6·12; *Comp. in* 100 *parts*, W, 79·31; O, 20·69.—Laurent considered that there were not fewer than six modifications of this acid, each of which formed a distinct class of salts; but the subsequent researches of Riche (*Ann. Chim. Phys.*, 1857, [3], l. 5), confirmed by those of Scheibler, appear to have shown that there are but two modifications in addition to the anhydride. These two different acids he terms *tungstic acid*, H_2WO_4, and *metatungstic acid*, $H_2W_4O_{13}$. De Marignac continues to apply the designation of *paratungstates* to a class of salts of the form of $5M_2O.12WO_3$, $(2n+1)\,OH_2$, or $M_5H.3W_2O_7.nOH_2$, although he has not isolated any specific modification of acid from them.

Tungstic anhydride may be obtained from calcic tungstate by the process already described, or by decomposing wolfram with aqua regia, evaporating to dryness, and dissolving the liberated tungstic acid in ammonia; the ammonic tungstate is purified by crystallization, and when heated in open vessels loses ammonia and water, and is converted into pure tungstic trioxide. This compound is a straw-yellow, tasteless, insoluble powder, which assumes a deeper orange tint when heated, the colour fading again as the temperature falls. In this form it is insoluble in acids, but is readily soluble in alkaline solutions, and when heated with solutions of the alkaline carbonates, it decomposes them with effervescence.

(963) **TUNGSTIC ACID**, H_2WO_4, is obtained in the form of a yellow powder by adding hydrochloric acid in excess to a boiling solution of the trioxide in any of the alkalies. The modification of acid thus obtained forms two classes of salts, one of which is normal, the other acid in composition. Even the normal salts all redden litmus faintly.* When mixed in the

* Scheibler (*Jour. pr. Chem.*, 1861, lxxxiii. 273) attributes to the tungstates formulæ much more complicated than those given by Riche; and De Marignac (*Ann. Chim. Phys.*, 1863, [3], lxix. 5) gives others for certain compounds yet more complicated than those of Scheibler, although the analyses of De Marignac agree almost exactly with Scheibler's.

The complexity of these formulæ has led Persoz to attempt to simplify them by altering the number assumed as the atomic weight of tungsten (*Ann. Chim. Phys.*, 1864, [4], i. 93). He calls the atomic weight of tungsten, 153·3, and

cold with an excess of hydrochloric acid, they are decomposed, and a white sparingly soluble hydrate of tungstic acid, $H_2WO_4.OH_2$, is deposited.

The following table contains the formulæ of a few of the tungstates, and shows their complex character:

Normal tungstates ...	$M_2O.WO_3$	or M_2WO_4
Paratungstates	$5M_2O.12WO_3.(2n+1)OH_2$	$M_5H.3W_2O_7.nOH_2$
Metatungstates	$M_2O.4WO_3nOH_2$	$M_2.W_4O_{13}.nOH_2$
Potassic tungstate ...	$K_2O.WO_3.2OH_2$	$K_2WO_4.2OH_2$
Sodic „ ...	$Na_2O.WO_3.2OH_2$	$Na_2WO_4.2OH_2$
Potassic paratungstate ...	$5K_2O.12WO_3.11OH_2$	$K_5H.3W_2O_7.5OH_2$
Sodic „ ...	$5Na_2O.12WO_3.27OH_2$*	$Na_5H.3W_2O_7.13OH_2$
Ammonic „ ...	$5(NH_4)_2O.12WO_3.11OH_2$	$(NH_4)_5H.3W_2O_7.5OH_2$
Ditto (crystallized hot)...	$5(NH_4)_2O.12WO_3.5OH_2$	$(NH_4)_5H.3W_2O_7.2OH_2$
Sodic potassic paratungstate	$4K_2O.Na_2O.12WO_3.15OH_2$	$K_4NaH.3W_2O_7.7OH_2$
Acid sodic tungstate ...	$3Na_2O.7WO_3.16OH_2$.	$Na_6H_8.7WO_4.12OH_2$
Potassic metatungstate ...	$K_2O.4WO_3.5OH_2$	$K_2W_4O_{13}.5OH_2$
Ammonic metatungstate and nitrate	$3(NH_4)_2O.8WO_3.N_2O_5.$ $4OH_2$	$(NH_4)_2W_4O_{13}.NH_4NO_3.$ $2OH_2$

Potassic tungstate is obtained by heating a strong solution of potassic carbonate nearly to its boiling-point, and adding tungstic anhydride so long as it produces an effervescence: long, slender, anhydrous, deliquescent needles of the tungstate are deposited from the solution as it cools; if redissolved, and allowed to recrystallize by spontaneous evaporation over oil of vitriol, at a temperature not exceeding 50° (10° C.), large limpid prisms, $K_2WO_4.2OH_2$ are formed; this salt is soluble in about half its weight of cold water. When pure, it is not decomposed by the addition of a solution of hydric sodic carbonate, but if silica be present, a precipitate is occasioned by this test. *Acid-tungstate of potassium* may be obtained as, $K_2W_2O_7$, by fusing the foregoing salt with tungstic anhydride, in the proportion of one molecule of each, or by adding tungstic anhydride, in the same proportion, to a hot solution of the normal salt, when it crystallizes in hydrated plates with OH_2. A sparingly soluble *paratungstate*, $K_5H3W_2O_7.5OH_2$, is obtained by passing a current of carbonic anhydride through a solution of the normal tungstate: it is deposited in pearly scales. The normal *sodic* tungstate, $Na_2WO_4.2OH_2$, crystallizes readily in thin pearly rhomboidal plates; it is used as a mordant in dyeing and calico-printing, and also for rendering

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if we take for this new weight the symbol Tu, the formula for the anhydride will be Tu_2O_5. But if Regnault's determination of the specific heat of tungsten be correct, it is improbable that this number represents that of the atomic weight; and indeed the formulæ which Persoz proposes, when reduced, as needful, for the larger atomic weight of oxygen, are not less complicated than those for which he attempts to substitute them. With one or two exceptions, the formulæ of De Marignac have been adopted as being the most symmetrical, and therefore the most probable, whilst they correspond quite as closely with the experimental results as any.

The researches of Graham (*Proc. Roy. Soc.*, 1864, xiii. 335), on the soluble colloids of the tungstic, molybdic, and other metallic acids, throw some further light upon their anomalies.

* De Marignac adopts the formula with $28OH_2$.

fabrics uninflammable: when treated with acetic acid it gives rise to acid salts, one of which, *sodic bitungstate*, $Na_2W_2O_7.6OH_2$, crystallizes in long prisms. The *paratungstate* of De Marignac, $Na_5H.3W_2O_7.13OH_2$, may also be obtained crystallized in large efflorescent oblique prisms. This salt becomes modified by long boiling of its solution, which then on evaporation deposits long 8-sided prisms of an acid salt, $Na_6H_8.7WO_4.17OH_2$. Another acid salt containing only 12 instead of $17OH_2$, is also known, and if either of these salts be fused at a full red heat, an insoluble salt, $Na_2O.4WO_3$, is left on treating the mass with water. No normal ammonic tungstate is known, but the *paratungstate* is easily obtained by digesting the anhydride in excess of ammonia: it is a sparingly soluble salt which at the ordinary temperature crystallizes in two distinct forms, either in delicate needles, or in thin brilliant plates, both having the same composition, $(NH_4)_5H.3W_2O_7.5OH_2$: if crystallized at a little below the boiling-point, it is deposited in hard, brilliant, rhomboidal needles which contain 2 instead of $5OH_2$.

The most important native ore of tungsten is *wolfram*, which occurs in hard prismatic crystals of a dark-brown colour; it is regarded as a mixture, in variable proportions, of ferrous and manganous tungstates. Its density is very high, being about 7·3. It was this circumstance that gave rise to the name *tungsten*, the term being a combination of two Swedish words, implying 'heavy stone.' This mineral is decomposed when boiled with hydrochloric acid, or with aqua regia, the tungstic acid remaining undissolved. It is also readily decomposed by fusion with nitre or with sodic carbonate, a soluble tungstate of the alkali-metal being formed.

(964) **METATUNGSTIC ACID**; $H_2W_4O_{13}$ or $W_4O_{12}.OH_2$.—The salts of this, the soluble modification of tungstic acid, colour litmus a wine-red, and generally crystallize with facility. When in solution they pass readily into the salts of tungstic acid; the change is gradual in neutral solutions at ordinary temperatures, more rapid in boiling liquids, or on the addition of a powerful acid, and the conversion is instantaneous if the hot liquid is mixed with an alkaline hydrate or carbonate in excess. The metatungstates are always prepared by the action of hydrated tungstic acid upon the tungstates.

If the white hydrated acid, $H_2WO_4.OH_2$, obtained by the action of hydrochloric acid in the cold upon the soluble tungstates, be neutralized by bases, it furnishes salts which are identical with the ordinary tungstates; but if one of the soluble normal tungstates, such as potassic tungstate, be boiled with the white hydrate of the acid in the proportion of a molecule of each until the solution no longer becomes turbid on the addition of an acid, a new salt, *potassic metatungstate*, $K_2W_4O_{13}.8OH_2$, is formed and is deposited in square based octahedra: a second salt containing only $5OH_2$ crystallizes in delicate needles, on adding alcohol to a strong solution of the first salt. A *sodic metatungstate* with $10OH_2$ crystallized in brilliant octahedra may be obtained by operating as for the first potash salt. *Ammonic metatungstate*, $(NH_4)_2W_4O_{13}.8OH_2$, crys-

tallizes in brilliant fusible octahedra. The metatungstates, when mixed with nitric acid, do not immediately yield a precipitate of the metallic acid.

Baric metatungstate, $BaW_4O_{13}.9OH_2$, may be obtained in shining quadratic octahedra, by mixing a warm concentrated solution of ammonic metatungstate with an equivalent quantity of one of baric chloride. A solution of metatungstic acid is obtained on decomposing baric metatungstate with its exact equivalent of dilute sulphuric acid.

De Marignac has found that when acid potassic tungstate is boiled with gelatinous silica, the liquid becomes alkaline, silica is dissolved, and a new salt, a *silico-tungstate*, is formed. The acid is unstable, but it may be obtained crystallized at ordinary temperatures in square tables, $4OH_2.SiO_2.12WO_3.29OH_2$; or in cubo-octahedra, which contain $18OH_2$, by evaporation at a rather high temperature. Two other silicated tungstic acids appear to exist: each of the three forms is soluble in alcohol, and forms very soluble salts with the alkali-metals. Scheibler, by the action of phosphoric acid on sodic tungstate, has obtained two *phosphotungstic acids* of complex formulæ.

(965) **OXYCHLORIDES OF TUNGSTEN.**—The *dioxydichloride*, WO_2Cl_2, may be obtained in yellow volatile crystalline scales, by passing dry chlorine, over either the tungstous oxide or tungstic anhydride heated to redness. It is sometimes termed chlorotungstic acid. The red volatile compound, formerly supposed to be a perchloride, is, according to Riche, an oxytetrachloride of the formula $WOCl_4$. (*Density of Vapour*, 10·74, Debray). It may be obtained by passing the vapour of the hexa- or pentachloride over the heated dioxide or dioxychloride. It forms ruby-red crystals which melt at 210°·4 (410°·7 F.) and volatilize at 227°·5 (441°·5 F.). Corresponding *oxybromides* exist.

(966) **SULPHIDES OF TUNGSTEN.**—There are two sulphides of this metal, the disulphide, and the trisulphide.

The *disulphide*, WS_2, *Density*, 6·26, was obtained by Riche in a pure form by heating, in a covered clay crucible, an intimate mixture of equal parts of acid potassic tungstate and sulphur. After fusion at a very high temperature for half an hour, the mass is poured out, powdered, and washed with boiling water. The disulphide is left in the form of bluish-black, slender needles, which feel unctuous to the touch, and stain paper or the skin, like plumbago; it admits of being consolidated by pressure, and might, probably, be used in the manufacture of drawing-pencils.

The *trisulphide*, WS_3, may be obtained by dissolving tungstic anhydride in a solution of dipotassic sulphide, and precipitating by the addition of an acid: it is slightly soluble in pure water.

The trisulphide is a strong sulphur acid, forming an orange-yellow crystallizable compound with dipotassic sulphide; the sulpho-salts may be formed by heating the tungstates of the alkali-metals with an excess of sulphur.

(967) **PHOSPHIDES OF TUNGSTEN.**—Phosphorus enters into combination with tungsten when its vapour is passed over the metal in a finely-divided state, and heated to redness in a glass tube; a dull, dark grey powder, W_2P_4, difficult of oxidation, is thus formed. Another compound, W_2P, is obtained in beautiful crystalline groups like geodes, by reducing a mixture of 2 molecules of phosphoric and 1 molecule of tungstic anhydride, at a very high temperature, in a crucible lined with charcoal: brilliant six-sided steel-grey prisms, of density 5·207, are thus obtained. It is a good conductor of electricity. It is oxidized with difficulty when heated, and is not attacked by acids.

(968) **Characters of the Salts of Tungsten.**—The compounds of this metal are not poisonous. No salts corresponding to tungstic dioxide are known.

The *tungstates* in solution are colourless. They are not precipitated either by *sulphuretted hydrogen* or by *ammonic hydric sulphide*. A *bar of tin*, placed in their acidulated solution in a vessel from which air is excluded, produces a deep violet-coloured liquid, owing to the reduction of the acid to a lower degree of oxidation. Zinc, stannous chloride, and other reducing agents, in the presence of acids, produce a like result. The addition of any stronger acid to a boiling solution of the tungstates causes the separation of a yellow precipitate of tungstic acid, which is soluble in phosphoric and in tartaric acid. On adding excess of concentrated hydrochloric acid to an alkaline tungstate, then potassic sulphocyanate, and afterwards metallic zinc, a deep rich green colour is produced; if the solution is dilute, the colour quickly changes to a deep amethyst. They yield *before the blow-pipe*, with borax, a colourless, transparent glass, which becomes yellow in the reducing flame, and blood-red on cooling. With microcosmic salt (678) they give a beautiful blue in the reducing flame, which becomes yellow or colourless in the oxidizing flame; the addition of a little metallic tin to the bead favours the production of the blue colour.

Tungsten is always estimated in the form of tungstic anhydride, 100 parts of which contain 79·31 of the metal.

§ VI. NIOBIUM or COLUMBIUM: Nb=94.

(969) **NIOBIUM** or **COLUMBIUM** was discovered in the year 1801 by Hatchett, who found it in a black mineral from Massachusetts, termed *columbite*. In the following year Ekeberg obtained a new metal, which he termed *tantalum*, from the *tantalite* and *yttro-tantalite* of Sweden.

These two metals were asserted by Wollaston to be identical —an opinion generally received until Rose showed that the American mineral contained a metallic oxide different from that furnished by tantalite: this oxide he termed *niobic acid;* and its metallic constituent, *niobium*, is the columbium of Hatchett. Rose at the same time stated that associated with this was a second metallic acid, which he termed the *pelopic*, but this he subsequently ascertained to be a compound of the metal niobium.

Metallic niobium is obtained by heating potassic fluoniobate,

$3KF.NbF_5$, with metallic sodium in an iron crucible. It is a black powder which burns when heated in the air, forming niobic oxide. It is dissolved by hydrofluoric acid, and by hot concentrated sulphuric acid.

(970) **NIOBIC CHLORIDE,** $NbCl_5$; *Theoretic Density of Vapour,* 9·39; *Observed,* 9·6; *Fusing-pt.* 194° (381°·2 F.); *Boiling-pt.* 240° (464° F.). —This is formed together with the oxychloride when a mixture of niobic oxide with charcoal is heated in a current of chlorine. It is yellow and fusible. The *oxychloride,* $NbOCl_3$, is white, and volatilizes without fusion.

(971) **NIOBIC OXYFLUORIDE,** $NbOF_3$, may be prepared by dissolving niobic oxide in hydrofluoric acid, and has also been obtained in the crystalline state by heating an intimate mixture of niobic anhydride and calcic fluoride in a current of hydrochloric acid gas. It forms compounds with the fluorides of many of the metals, analogous to the titanofluorides. Five *potassic nioboxyfluorides* exist, and of these the compound, $2KF.NbOF_3$, when dissolved in hot hydrofluoric acid, deposits *potassic fluoniobate,* $3KF.NbF_5$, in lustrous monoclinic needles. When treated with potassic carbonate it is decomposed, yielding potassic niobate.

(972) **NIOBIC OXIDE,** *Niobic anhydride,* or *Niobic acid;* $Nb_2O_5 = 268$; *Density,* 4·5.—This oxide is formed when the metal is burnt in the air, and may also be obtained in the pure state by decomposing the chloride or oxychloride with water. Niobic oxide is generally separated from columbite and the other minerals containing it, by fusing them with acid potassic sulphate in a platinum crucible, removing the soluble salts from the fused mass by washing it with hot water, and the tin and tungsten from the residue by means of ammonic sulphide. The residue after being exhausted by boiling with concentrated hydrochloric acid to remove iron, &c., is washed with water, and the mixture of niobic and tantalic acids thus obtained is treated with hydric potassic fluoride, KF.HF, which dissolves the niobium as oxyfluoride, $2KF.NbOF_3$, whilst the tantalum is left as a sparingly soluble potassic fluotantalate, $2KF.TaF_5$.

Niobic oxide is a white powder, which becomes yellow when heated. It is of the nature of an acid anhydride, combining with basic oxides to form a class of compounds called niobates. The potassic niobates, of which several appear to exist, crystallize readily, but their composition has not yet been satisfactorily settled. When alkaline niobates are decomposed by acids they yield *niobic hydrates.*

§ VII. TANTALUM: Ta = 182.

(973) **TANTALUM.**—This rare metal occurs associated with niobium in tantalite, niobite, tapiolite, samarskite, and several other minerals, and with yttrium, cerium, &c.; in polycrase, euxenite, yttrotantalite, &c. It is also found in pyrochlore and woehlerite. The metal may be obtained by a process similar to that employed for the preparation of niobium, by heating potassic fluotantalate with metallic sodium in a well-closed iron crucible. It is a black powder, closely resembling niobium in appearance and properties. When the fluotantalate is fused with aluminium in a crucible lined with carbon, a button is obtained, which on treatment with hydro-

chloric acid leaves a compound of tantalum and aluminium, $TaAl_3$, as a crystalline powder of density 7·0.

(974) **TANTALIC CHLORIDE**, $TaCl_5 = 359·5$.—This compound is formed on heating metallic tantalum, or an intimate mixture of tantalic acid and carbon in a current of dry chlorine. It is a pale yellow crystalline substance which melts at 211°·3 (412°·3 F.) and boils at 242° (467°·6 F.).

(975) **TANTALIC FLUORIDE**, $TaF_5 = 277$, is obtained on dissolving tantalic acid in aqueous hydrofluoric acid. It unites with the alkaline fluorides to form fluotantalates; *potassic fluotantalate*, $KF.TaF_5$, crystallizes in monoclinic prisms isomorphous with the corresponding niobium compound.

(976) **OXIDES OF TANTALUM.**—Tantalum appears to form two oxides, one of these, *tantalous oxide* or *dioxide*, TaO_2, is said to be obtained on exposing tantalic oxide to an intense heat in a crucible lined with charcoal. It is a dark-grey mass hard enough to scratch glass, and which becomes converted into tantalic oxide when heated in contact with air.

Tantalic oxide, TaO_5, density 7·1 to 8·2, resembles niobic oxide. It may be obtained from tantalite by fusing it with potassic hydrate, and precipitating the solution with hydrochloric acid: the hydrated tantalic acid is then converted into the anhydride by ignition. Like niobic oxide it forms with the basic oxides a class of compounds called tantalates, of which the alkaline salts are soluble in water, whilst those of the earth-metals and heavy metals are insoluble.

Tantalic oxide yields *tantalic nitride* when heated in dry ammonia, whilst with carbonic bisulphide at a red heat, *tantalic sulphide* is formed.

Niobium and tantalum belong rather to the group of phosphorus than to that of silicon, and the same remark applies to vanadium.

Hermann supposed the yttro-tantalite of Siberia to contain a new metal, analogous to columbium, to which he gave the name of *Ilmenium*; but he has since proved the so-called ilmenic acid to be a mixture of the tantalic and niobic anhydrides.

§ VIII. VANADIUM: V=51·3.

(977) **VANADIUM** is one of those rare metals at present known only as chemical curiosities: it was discovered, in 1830, by Sefström, in a Swedish iron ore from Taberg, which yielded bar iron remarkable for its malleability; but its most abundant ore is *vanadinite*, $3Pb_32VO_4.PbCl_2$, a mineral isomorphous with pyromorphite, $3Pb_32PO_4.PbCl_2$; vanadinite has been found at Zimapan in Mexico, at Wanlockhead in Scotland, and more recently in Chili; Wöhler, Wälz, and Stillwell have also found vanadium accompanying some of the ores of uranium and iron. Quite recently a more abundant supply of this metal has been met with by Roscoe in the cupriferous stratum of the new red sandstone at Alderley Edge in Cheshire, and we are indebted to the last-named chemist for a new and extended investigation of the principal compounds of vanadium.

Berzelius believed that he had isolated the metal by heating vanadic anhydride in a covered porcelain crucible with potassium,

but the brilliant metallic-looking powder, according to Roscoe, still retains oxygen. Several anomalies have been cleared up by this discovery, as vanadium now takes its place in the series of phosphorus, with which it forms isomorphous compounds, instead of being, as was formerly supposed, allied to molybdenum and tungsten. The metal may be obtained by heating perfectly pure vanadic dichloride to redness for 40 to 80 hours in a stream of pure and dry hydrogen; as thus prepared it contains hydrogen, and under the microscope appears as a silvery-white crystalline mass. It is permanent in the air at ordinary temperatures, but decomposes water at 100° (212° F.); it burns with vivid scintillations when the powdered metal is thrown into a flame.

(978) **VANADIUM CHLORIDES.**—Three of these compounds have been obtained, VCl_2, VCl_3, and VCl_4, the latter, *vanadic tetrachloride*, is a reddish-brown, volatile liquid, boiling at 154° (309°·2 F.), and having a density of 1·8584 at 0° (32° F.). It is prepared by heating metallic vanadium or vanadic mononitride to redness in a current of chlorine. By boiling, it is resolved into free chlorine and the *trichloride*, a substance crystallizing in shining tables of a beautiful peach blossom colour. The *dichloride* is prepared by passing the vapour of the trichloride, mixed with hydrogen, through a tube heated to dull redness. It crystallizes in bright, apple-green, micaceous plates.

Vanadium Bromide, VBr_3, corresponding to the trichloride has also been prepared; it is obtained as a greyish-black, amorphous mass on passing bromine vapour over heated vanadium nitride. It is very unstable and deliquescent: heated in contact with the air it gives off bromine and leaves the pentoxide.

(979) **OXIDES OF VANADIUM.**—Five oxides of the metal are known, namely, V_2O, V_2O_2, V_2O_3, V_2O_4, and V_2O_5. The oxide, V_2O_2, according to Roscoe, is the body regarded by Berzelius as the metal; V_2O_3 was his vanadous oxide VO, V_2O_4 was his vanadic oxide VO_2, and the anhydride V_2O_5, his vanadic acid VO_3.

The *monoxide*, V_2O, is formed by long exposure of metallic vanadium to the air at ordinary temperatures, or more rapidly at a dull red heat. It is a brown powder, which easily passes to a higher state of oxidation.

Salts of the oxide, V_2O_2 (the *vanadyl* of Roscoe), are lavender-coloured in solution. Roscoe obtains them by reducing a dilute solution of the anhydride in sulphuric acid, by means of zinc, cadmium, or sodium amalgam. The solution absorbs oxygen from the air with great avidity, and owing to its deoxidizing power it bleaches indigo and litmus as quickly as chlorine itself, but the colour returns on exposure to the air. The oxide has been obtained as a bright grey metallic-looking powder by passing a current of dry hydrogen charged with the vapours of the oxychloride, $VOCl_3$, through a tube containing ignited charcoal. It forms a light grey metallic-looking powder of density 3·64. When heated to redness in the air, it takes fire and burns to the black oxide. It is soluble in dilute acids with evolution of hydrogen.

The *sesquioxide*, $V_2O_3 = 150·6$, *density* 4·72, is obtained from vanadic anhydride, by reducing it, by means of a stream of hydrogen, or by charcoal: it is a black, crystalline, brittle mass, resembling graphite in appearance, and, like it, conducts electricity. Roscoe states that the presence of a minute quantity of phosphoric acid prevents the complete reduction of the anhydride by hydrogen.

to this condition. In this form it does not combine either with acids or with bases. Salts corresponding to the sesquioxide, V_2O_3, of a brown or green colour according as they are neutral or acid, may be obtained by reducing the sulphate of vanadic anhydride by means of magnesium, which only carries the reduction to this stage.

If the sesquioxide is heated in air for some time, it absorbs oxygen, forming *hypovanadic oxide* or *divanadium-tetroxide*, $V_2O_4 = 166{\cdot}6$, as a black anhydrous powder, and even at common temperatures this absorption of oxygen goes on until the mass becomes converted into blue crystals of the same oxide: it may also be obtained by heating the oxychloride, $V_2O_4Cl_2$, to redness in an atmosphere of carbonic anhydride.

The oxide, V_2O_4, dissolves in acids, and forms salts with them which have a blue colour; these when mixed with a solution of sodic carbonate furnish a grey hydrate of this oxide, $V_2O_4.OH_2$; in this form it rapidly absorbs oxygen, and becomes first brown and then green.

Solutions of divanadium tetroxide may be obtained by reducing the solution of sulphate of vanadic acid by sulphuretted hydrogen or sulphurous acid, when a bright blue liquid is obtained.

Hypovanadic trisulphate, $V_2O_4.3SO_3.6OH_2$, may be prepared in this way by dissolving pure vanadic anhydride in concentrated sulphuric acid, reducing with sulphurous acid solution and evaporating; the trisulphate is thus obtained as a blue crystalline powder. Another hydrate, $V_2O_4.3SO_3.4OH_2$, is deposited in the crystalline state on adding concentrated sulphuric acid to a solution of the sulphite When the trisulphate is treated with absolute alcohol, one-third of the acid is removed, and *hypovanadic disulphate* is left as a deliquescent blue powder of the formula, $V_2O_4.2SO_3.7OH_2$. Hypovanadic oxide also appears to possess feeble acid properties, for it forms compounds with bases. Crow (*Jour. Chem. Soc.*, 1876, ii. 458) has isolated the following:

Potassic hypovanadate	$K_2V_4O_9.V_2O_4.7OH_2$
Sodic hypovanadate	$Na_2V_2O_5.V_2O_4.7OH_2$
Ammonic hypovanadate	$(NH_4)_2V_2O_5.V_2O_4.3OH_2$
Baric hypovanadate	$BaV_2O_5.V_2O_4.5OH_2$
Plumbic hypovanadate	PbV_2O_5
Argentic hypovanadate	$Ag_2V_2O_5$

Vanadic anhydride, $V_2O_5 = 182{\cdot}6$; *density*, 3·49, is of a brownish-red colour; at a red heat it fuses without further change, and crystallizes in rhombic prisms on cooling, becoming incandescent in the act of passing from the vitreous to the crystalline condition. It is sparingly soluble in water, to which it communicates a yellow tint: the solution is powerfully acid and reddens litmus strongly. It forms tetrabasic *pyrovanadates*, $M_4V_2O_7$, *metavanadates*, MVO_3, *orthovanadates* with three of basyl, M_3VO_4, and anhydro or acid salts, bearing a close analogy to the different classes of phosphates. The normal salts when first prepared are yellow; in a few hours, however, especially if gently warmed, they are changed into white isomeric salts. The most important of the metavanadates is *ammonic vanadate*, NH_4VO_3, from which the acid itself is usually obtained. Ammonic vanadate is procured by putting pieces of ammonic chloride into a crude solution of potassic vanadate (such as is prepared by the deflagration of the slag obtained from the iron ore of Taberg with nitre, after the excess of alkali has been neutralized with hydrochloric acid): ammonic vanadate being insoluble in a saturated solution of ammonic chloride is then gradually deposited in small crystalline grains. Cold water dissolves it sparingly, but it is much more soluble in hot water: when heated in the open air the ammonia is expelled, and pure vanadic anhydride is left. The *acid ammonic*

vanadate, $2(NH_4VO_3).V_2O_5$, yields crystals of an orange colour. If mixed with tincture of galls, these salts give a deep black liquid, which preserves its blackness even when much diluted: it forms a very permanent writing ink, since it is not destroyed either by acids, which turn it blue, or by alkalies, or by chlorine.

The orthovanadates are usually less stable than the pyrovanadates, *sodic orthovanadate*, Na_3VO_4, splitting up in solution into sodic hydrate, and *sodic pyrovanadate*, $Na_4V_2O_7$; this crystallizes in beautiful hexagonal tables which are easily soluble in water, but insoluble in alcohol: the *plumbic* and *argentic orthovanadates* are insoluble, the former being yellow and the latter orange-coloured. *Argentic pyrovanadate*, $Ag_4V_2O_7$, is thrown down as a yellow, dense, crystalline precipitate on mixing solutions of sodic pyrovanadate and argentic nitrate.

Metavanadic acid, HVO_3, may be obtained by mixing a cold saturated solution of cupric sulphate with one of ammonic chloride in large excess, then adding a saturated solution of ammonic vanadate until a permanent precipitate begins to appear; on heating slowly to 75° (167° F.) the acid is deposited in golden scales.

Vanadic anhydride appears to combine in different proportions with the inferior oxides of the metal, forming compounds which are either of a green or a purple colour. It also combines with many acids in definite proportions, such as the sulphate, $V_2O_5.3SO_3$. Several of these compounds crystallize with facility.

(980) **VANADIC OXYCHLORIDES.**—According to Roscoe several oxychlorides exist, viz., V_2O_2Cl, $VOCl$, $VOCl_2$, and $VOCl_3$. The most important is the oxytrichloride, which was formerly regarded as the trichloride.

Vanadic Oxytrichloride, $VOCl_3$; *Theoretic Density of Vapour*, 6·0066; *Observed*, 6·108; *of liquid*, 1·841 *at* 14°·5 (58° F.); *Boiling-pt.* 126°·7 (260° F.); *Rel. wt.* 86·9; *Mol. Vol.* [ ]; *Mol. wt.* 173·8.—This is a yellow, fuming, volatile liquid analogous to phosphoryl chloride, $POCl_3$. It is immediately decomposed by water into vanadic and hydrochloric acids; $VOCl_3 + 3OH_2 = H_3VO_4 + 3HCl$. This oxychloride may be obtained by heating a mixture of vanadic anhydride and charcoal in a current of hydrogen, after which it is heated in a current of dry chlorine; or it may be procured at once by passing dry chlorine over the sesquioxide, $3V_2O_3 + 6Cl_2 = V_2O_5 + 4VOCl_3$. This oxychloride remains liquid at −15° (5° F.).

Vanadic oxytrichloride is decomposed, if heated with hydrogen, lower solid oxychlorides being formed.

Vanadic Oxydichloride, or *Hypovanadic chloride*, $VOCl_2$, is also formed when pure vanadic pentoxide or vanadic oxytrichloride is dissolved in concentrated hydrochloric acid, and the resulting green solution reduced by sulphuretted hydrogen. On evaporation, the dichloride, $VOCl_2$, is left as a brown, deliquescent amorphous mass which dissolves in water, yielding a brown solution.

Oxybromides, corresponding to these chlorine compounds, are known.

(981) **VANADIUM NITRIDES.**—Two of these are known, VN and VN_2. The *dinitride*, VN_2, is obtained as a black powder by passing ammoniacal gas over the oxytrichloride, heating to expel ammonic chloride, washing with solution of ammonia, and drying over sulphuric acid. The other nitride, VN, may be obtained as a steel-white, brittle compound, by igniting the foregoing compound intensely in a current of dry ammonia, or more conveniently, by passing a current of dry ammonia over ammonic vanadate at a white heat.

(982) **Characters of the Compounds of Vanadium.**—1.—The salts corresponding to the *divanadium tetroxide*, V_2O_4, yield blue solutions, which give a deep blue-black colour with *tincture of galls*, and a grey precipitate with the

alkaline hydrates, soluble in excess of the precipitant; the precipitate becomes red by exposure to the air. *Potassic ferrocyanide* gives a yellow precipitate, which becomes greenish when exposed to the air. The *sulphides* of the alkali-metals give a brownish-black precipitate, readily soluble in excess, and forming a magnificent purple liquid.

2.—The *vanadates* are usually red or yellow: they have a powerfully astringent taste: when treated either with sulphuretted hydrogen, or sulphurous acid, or when boiled with sulphuric acid and either alcohol or sugar, they give a beautiful blue solution, a reaction that distinguishes them from the chromates, which under these circumstances furnish a green liquid. *Before the blowpipe* in the reducing flame, compounds containing vanadium give with borax a green glass, which becomes yellow in the oxidizing flame.

§ IX. ARSENICUM: As‴=75.

(983) **ARSENICUM**: *Theoretic Density of Vapour*, 10·38; *Observed*, 10·6; *of solid, from* 5·395 to 5·959; *Atomic Vol.* ½ or □; *Rel. wt.* 150; *Molecular Vol.*, As_4 □□;* *Triad, as in* $AsCl_3$; *rarely Pentad, as in* $As(CH_3)_4I$.—Arsenicum, or *arsenic*, in various states of combination, was known to mankind before the Christian era. This element presents many analogies with phosphorus, and with nitrogen: it is considered by many chemists to belong to the non-metalic elements. It, however, conducts electricity with facility, and possesses a high metallic lustre. Arsenicum generally presents itself in the form of a combination with some other metal, especially with iron, or with cobalt, nickel, copper, or tin. It is occasionally found in the native state, and it sometimes occurs united with oxygen and certain metals, constituting arseniates, such as those of iron, copper, and lead. More rarely it occurs united with sulphur, either as the red sulphide, As_2S_2, realgar, or as the yellow sesquisulphide, As_2S_3, known as orpiment.

The greater part of the arsenic of commerce is derived from mispickel, FeAsS, an arsenical sulphide of iron furnished abundantly by the Silesian mines, and from the arsenides of nickel and cobalt, which yield arsenious sesquioxide as a secondary product in the ordinary process of working these ores. The separation of the arsenic is effected by roasting the mineral in a manner similar to that employed for driving off sulphur: but the arsenious sequioxide which is produced, being less volatile, more valuable, and more deleterious, is condensed in large chambers, through which the flues from the furnace pass. The

* Four atoms of arsenicum enter into the formation of one molecule of its vapour; in this respect this element corresponds with phosphorus.

emptying of these chambers, which is performed about once in six weeks, is an operation attended with danger to the workmen, from the poisonous and irritating nature of the finely-powdered arsenious sesquioxide. In order in some degree to protect the men whilst thus engaged, they are cased in leather, with glazed apertures for the eyes, and are made to cover their mouths and nostrils with damp cloths, which arrest most of the acrid particles. Much of the sesquioxide obtained from these chambers is in the form of a fine powder; it is still very impure, and it is therefore again sublimed in iron pots, the upper part of which is kept moderately cool; here it is condensed as a transparent, half-fused, vitreous mass. The lower portions only of this sublimate are pure, and these are sold as white arsenic; the upper are either resublimed, or are employed for the purpose of furnishing arsenicum. In order to obtain the metal, the sublimed sesquioxide is powdered, mixed with charcoal, or with twice its weight of black flux, and heated in an earthen crucible, upon the top of which a second inverted crucible is luted, and screened from the fire by means of a perforated iron plate. The reduced metal is condensed in the upper crucible.

Properties.—Metallic arsenic, or *arsenicum*, has a brilliant, dark steel-grey lustre; it is very brittle, and is easily reduced to powder. When heated a little above 100° (212° F.) under the ordinary pressure it gives a luminous cloud, resembling phosphorus in this respect; at 180° (356° F.) in closed vessels, it begins to volatilize without fusing, and crystallizes indistinctly, as it is condensed, in rhombohedra, which are isomorphous with those of antimony. Under pressure, however, it fuses at a temperature between the melting points of antimony and silver: the solidified metal has a steel-grey colour and brilliant lustre. Its density at 19° (66°·2 F.) is 5·709. The vapour of arsenic is colourless, and possesses a powerful, oppressive, alliaceous odour. The metal may be exposed to dry air without undergoing change, but in a moist state it is slowly oxidized, and a substance known as *fly-powder* is formed; it is probably a mixture of arsenious sesquioxide and arsenicum, though it is regarded by some chemists as a suboxide. If the metal be heated in open vessels it absorbs oxygen, burns with a lurid bluish flame, and is converted into arsenious anhydride, which is condensed upon cool bodies in the neighbourhood as a white mealy powder. When thrown in fine powder into chlorine gas, it takes fire spontaneously, and is converted into arsenious chloride. Bromine, iodine, and sulphur also combine readily with arsenicum when aided by a gentle

heat. Nitric acid easily oxidizes the metal, and converts it into arsenic acid; if deflagrated with nitre, it is converted into potassic arsenate. Hydrochloric acid exerts but little action on the metal, but if the hydrochloric be mixed with nitric acid, or with potassic chlorate, the metal is rapidly converted into arsenic acid.

A small quantity of arsenic is added to lead to facilitate its assuming the globular form in the manufacture of shot. In the form of arsenious sesquioxide it is extensively used in the preparation of green and yellow pigments; it is likewise employed to prevent smut in grain, but the practice is to be reprobated; it is also used in the manufacture of flint glass as an oxidizing agent, for converting the ferrous oxide into ferric oxide, in order to get rid of the green tinge which ferrous oxide communicates to the vitreous mass. Its employment as a poison for vermin has often been made a pretext for procuring it for criminal purposes.

(984) **COMPOUNDS OF ARSENICUM WITH HYDROGEN.**—It has been stated that arsenic forms two combinations with hydrogen, but one of these, a solid of a chestnut-brown colour obtained by employing a plate of arsenicum as the platinode during the voltaic decomposition of acidulated water, formerly supposed to be a hydride of arsenic, As_4H_2, is merely metallic arsenic. A similar substance is obtained by the action of hypophosphorous acid on a solution of arsenious anhydride in hydrochloric acid. The other is a gaseous body, AsH_3, of considerable importance; it corresponds in composition to the gaseous phosphuretted hydrogen.

(985) **TRIHYDRIDE OF ARSENICUM;** *Arseniuretted hydrogen*; $AsH_3 = 78$; *Rel. wt.* 39; *Theoretic Density*, 2·6988; *Observed*, 2·695; *Mol. Vol.* [ ].—This remarkable gaseous compound is an exceedingly poisonous body; it is colourless, and has a disagreeable alliaceous odour; it is sparingly soluble in water, and possesses neither acid nor alkaline properties. It consists of half a volume of arsenical vapour and 3 volumes of hydrogen condensed into 2 volumes.

The composition of the gas may be thus represented

			By weight.		By volume.
Arsenic	As	=	75 or 96·15	...	0·5
Hydrogen	H_3	=	3 3·85	...	3·0
	AsH_3	=	78 100·00		2

By a temperature of −30° (−22° F.), it is reducible to a limpid colourless liquid, which remains fluid at −110° (−166° F.),

Arseniuretted hydrogen is inflammable, and burns with a bluish-white flame, which deposits arsenicum upon cold bodies introduced within it, and arsenious anhydride upon those held above. It is also decomposed when caused to pass through tubes heated to a temperature a little short of redness, arsenicum being deposited as a steel-grey crust, whilst hydrogen gas escapes: if a current of dry sulphuretted hydrogen be passed over the heated crust, a yellow sublimate of orpiment is formed, which is not acted on by a current of dry hydrochloric acid gas. These reactions distinguish the arsenical from the antimonial crust, which by similar treatment gives a dark orange-coloured sulphide decomposable by a current of dry hydrochloric acid gas. Chlorine decomposes arseniuretted hydrogen with flame, forming hydrochloric acid, and causing the deposition of arsenic as a brown powder. Concentrated nitric acid also absorbs the gas completely, whilst arsenic acid is formed. The gas is entirely absorbed by a solution of cupric sulphate, sulphuric acid being liberated, whilst arsenide of copper is precipitated. Argentic nitrate is also decomposed by arseniuretted hydrogen, arsenic acid being formed and silver precipitated; $AsH_3+8AgNO_3+4OH_2=8HNO_3+H_3AsO_4+4Ag_2$. In the application of Marsh's test (p. 741) the presence of a small quantity of nitric acid prevents the formation of the gaseous hydride, the arsenic being precipitated in the solid state. Solution of corrosive sublimate likewise dissolves the gas completely, a compound of calomel and arsenide of mercury being formed. It is also largely absorbed by oil of turpentine, with which it forms a crystalline compound.

Pure arseniuretted hydrogen may be prepared by decomposing arsenide of zinc with sulphuric acid diluted with three parts water. Arsenide of zinc is obtained by heating equal weights of powdered arsenicum and granulated zinc in an earthen retort; the fused mass is removed by breaking the retort, and is subsequently reduced to powder. The greatest care is required not to inhale any of this deadly gas.

When arseniuretted hydrogen is caused to act on phosphorous trichloride, mutual decomposition takes place and a phosphide of arsenic, PAs, is produced with evolution of hydrochloric acid (Janoffsky, *Deut. chem. Ges. Ber.*, 1875, viii. 1636).

(986) **ARSENIOUS CHLORIDE**, or *Trichloride of arsenic*; $AsCl_3=181{\cdot}5$; *Rel. wt.* 90·75; *Theoretic Density of vapour*, 6·2799; *Observed*, 6·3; *of liquid at* 0° (32° F.), 2·205; *Boiling-pt.* 132° (269·°6 F.); *Mol. Vol.* [ ].—Only one compound of arsenic with chlorine is known. It is produced either by the combustion

of the metal in chlorine, or by distilling a mixture of 1 part of arsenicum and 6 parts of corrosive sublimate, or still more easily by heating arsenious anhydride in a current of dry chlorine gas; it condenses as a heavy, colourless, oily-looking liquid, which remains fluid at $-29°$ ($-20°{\cdot}2$ F.); it fumes when exposed to the air, and is immediately decomposed by water into arsenious and hydrochloric acids.

A tribromide, $AsBr_3$, may be formed by analogous means; it forms deliquescent, colourless prisms of density 3·66, which melt at 20° (68° F.); it boils at 220° (428° F.)

(987) **ARSENIOUS IODIDE**, or *Tri-iodide of arsenic*, $AsI_3 = 456$; *Theoretic Density of vapour*, 15·777; *Observed*, 16·1; *of solid*, 4·39; *Mol. Vol.* [ ]; *Rel. wt.* 228.—This may be prepared by subliming a mixture of 3 parts of iodine and 1 part of the metal in a flask; it forms brick-red, brilliant flakes. It may also be obtained by digesting 3 parts of powdered arsenicum and 10 of iodine in 100 of water, or by dissolving arsenious anhydride in hydriodic acid; on evaporation, the clear liquid yields red hydrated crystals which are soluble in alcohol, and which become anhydrous when heated to their fusing-point.

(988) **ARSENIOUS TRIFLUORIDE**, AsF_3, may be prepared by distilling 5 parts of fluor-spar, mixed with 4 of arsenious anhydride and 10 of concentrated sulphuric acid. It is a fuming, colourless liquid, which corrodes glass rapidly, and is decomposed by water, yielding arsenious anhydride and hydrofluoric acid. It boils at 63° (145°·4 F.), and has a density of 2·73.

(989) **OXIDES OF ARSENIC.**—These are two in number: the sesquioxide or arsenious anhydride, As_2O_3, and arsenic anhydride, As_2O_5; both form acids, no basic oxide being known.

(990) **ARSENIOUS ANHYDRIDE**, *Arsenious acid*, or *Arsenious sesquioxide*; $As_2O_3 = 198$; *Theoretic Density of vapour*, 13·701; *Observed*, 13·85; *Comp. in* 100 *parts*, As, 75·76; O, 24·24; *Mol. Vol.* $(As_2O_3)_2 = [\ ]$.;* *Rel. wt.* 198.—This compound is the *white arsenic* of the shops. It is prepared upon the large scale during the roasting of arsenical ores in the manner already described. It exists in two modifications, a vitreous and a crystalline form. When purified by resublimation and freshly obtained, it is in semi-transparent, vitreous, lamellated masses; but by exposure to the air, it gradually becomes opaque, and of a yellowish-white colour. This change advances slowly, from the exterior towards the interior, so that the mass is often opaque at the surface whilst it remains transparent in the centre. Both varieties of arsenious anhydride are freely soluble in hot hydrochloric acid, and when

* The molecular volume of this body is anomalous, the density of its vapour being double of that which might from analogy have been expected.

the solution is boiled, a portion of the arsenic is volatilized in the form of trichloride; as the liquid cools the excess crystallizes in transparent, anhydrous octahedra, consisting of uncombined arsenious sesquioxide; but when the transparent variety has been employed, the formation of each crystal is marked by the emission of a flash of light which is perceptible in a darkened room. The opaque variety exhibits no such phenomenon in crystallizing from its solution. A hot solution of ammonia also dissolves white arsenic freely, and deposits it in anhydrous octahedra of the uncombined sesquioxide on cooling, mixed with prismatic crystals of ammonic arsenite, $NH_4.AsO_2$ (Bloxam, *Jour. Chem. Soc.*, 1862, xvi. 297). Guibourt found the opaque variety to have a density of 3·699; it is less dense than the transparent form, the specific gravity of which he states to be 3·7385. The two varieties also differ in their solubility: according to Bussy, water dissolves nearly three times as much of the transparent as of the opaque form: Buchner gives 1 part in 355 and 108 parts of cold water respectively. A cold saturated solution of the vitreous variety gradually deposits its excess in the form of the opaque anhydride, and retains between 1·3 and 3 per cent. in solution; the liquid reddens litmus. Mere grinding to a fine powder converts the transparent into the opaque variety, and reduces its solubility. Heat, however, gradually reconverts the opaque into the vitreous modification, so that long-continued boiling renders the opaque as soluble as the vitreous form. It is therefore difficult to state the precise degree of solubility of either form of the compound, because the two varieties are liable to be formed in varying proportion in the course of an experiment. The largest proportion which water will dissolve at 100° (212° F.) is between 11 and 12 per cent., but it dissolves readily in water at 250° (482° F.): it is also very soluble in glycerine. Both nitric acid and aqua regia dissolve the sesquioxide, and convert it into arsenic acid.

Arsenious sesquioxide, when heated to about 193°·3 (380° F.), softens and is sublimed without fusing, being condensed in transparent octahedra upon warm surfaces, but it occasionally forms long prismatic needles, isomorphous with those of antimonious oxide, Sb_2O_3. Its vapour is without odour; it is colourless, and contains 1 volume of vapour of arsenic and 3 volumes of oxygen, condensed into 1 volume. When distilled with hydrochloric acid, arsenious anhydride is converted into arsenious chloride, which passes over with the distillate.

(991) **Arsenites.**—Arsenious anhydride is soluble in solu-

tions of the alkaline hydrates and carbonates: with potassium and sodium it forms soluble compounds which do not crystallize if the alkali be in excess; the acid *monopotassic salt*, $2KH_2AsO_3.As_2O_3$, however, may be obtained in rectangular prisms. Its acid properties are feebly marked, but it appears to be tribasic, the most usual formula of its salts being M'_3AsO_3 (Bloxam). A solution of *tripotassic* arsenite has been used medicinally for many years under the name of *Fowler's solution*. The arsenites of the metals of the earths (particularly tricalcic diarsenite) are nearly insoluble in water, but are readily dissolved by acids. *Hydric cupric* arsenite, $CuHAsO_3$, is, in a commercial point of view, the most important of these salts; it is of a delicate and beautiful green colour, constituting the pigment sold under the name of *Scheele's green*. It is prepared by dissolving 1 part of arsenious anhydride and 3 parts of potassic carbonate in 14 of water, and adding the liquid to a boiling solution of 3 parts of cupric sulphate in 40 of water; the shade of green may be varied by altering the proportion of arsenious anhydride. This compound is a dangerous poison, but being a cheap and brilliant colour is, as well as Schweinfurt green, largely used for paper-hangings; this custom cannot be too strongly reprehended. It is soluble in acids and in ammonia. When heated it is partially decomposed, and arsenious anhydride sublimes. The *Schweinfurt green*, which is also used largely as a pigment, is a cupric arsenite and acetate, $3CuAs_2O_4.Cu2C_2H_3O_2$, made by mixing equal parts of arsenious anhydride and cupric acetate, in solution at a boiling temperature, adding an equal bulk of cold water, and allowing the mixture to stand for some days. *Triargentic* arsenite, Ag_3AsO_3, is of a canary-yellow colour; it is obtained by the addition of a solution of argentic nitrate to one of tripotassic arsenite. If a slip of bright copper foil be introduced into a solution of arsenious acid in hydrochloric acid, a grey film of reduced arsenicum is deposited on the copper; if zinc be substituted for copper, arseniuretted hydrogen is evolved (985). Arsenious acid in solution may readily be converted into arsenic acid by acidulating the liquid with hydrochloric acid, warming it, and gradually adding potassic chlorate in small quantities; when, however, arsenic acid is distilled with concentrated hydrochloric acid, chlorine is evolved, and arsenious chloride is found in the distillate. Arsenious acid is indeed a powerful reducing agent; its solution in hydrochloric acid reduces auric chloride; it bleaches potassic permanganate, and reduces potassic dichromate to a chromic sesquisalt.

If a solution of arsenious acid in sodic carbonate be mixed with a little starch, and a solution of iodine or chlorine be added until the starch turns blue, the arsenious is converted into arsenic acid; this reaction forms the basis of a volumetric process for the determination of iodine and chlorine in solution.

If a minute fragment of arsenious sesquioxide be heated with a similar portion of sodic acetate in a small test-tube, the characteristic and peculiarly offensive odour of kakodyl is perceived.

(992) **ARSENIC ANHYDRIDE**, or *Arsenic acid;* $As_2O_5=230$; *Comp. in* 100 *parts*, As, 65·22; O, 34·78.—This compound is obtained by treating arsenious sesquioxide with nitric acid in slight excess, and then boiling down to dryness in a platinum vessel. A white, somewhat deliquescent mass of arsenic anhydride remains: by slow evaporation of its solution arsenic acid may be obtained in hydrated crystals.

E. Kopp (*Ann. Chim. Phys.*, 1856, [3], xlviii. 106) found, when operating on a large scale, that if a concentrated solution of the acid was stirred briskly at a temperature not exceeding 15° (59° F.), a semi-liquid mass was often obtained, filled with elongated prisms or rhomboidal plates, $As_2O_5.4OH_2$, which are extremely deliquescent; when heated to 100° (212° F.) they become liquid, lose water, and gradually deposit a white creamy mass, consisting of small needles; these, when dried by pressure between folds of filtering-paper, were found to consist of $As_2O_5.3OH_2$, or H_6AsO_4. In order to obtain the hydrate, $As_2O_5.2OH_2$, or $H_4As_2O_7$, Kopp evaporated at a temperature ranging between 140° and 180° (284° and 356° F.); if a very concentrated solution of this so-called hydrate be kept for some time at 200° (392° F.), and then be gradually raised to 206° (402°·8 F.), the liquid suddenly boils up, becomes pasty, and is converted into a pearly mass of dazzling whiteness, consisting of $As_2O_5.OH_2$, or $HAsO_3$, which it is difficult to obtain free from the anhydride. At a temperature below redness it becomes anhydrous; all these different forms when dissolved in water, reproduce a liquid like the original solution. In preparing arsenic acid, Kopp employs 300 kilos. of nitric acid, density 1·35, to 400 kilos. of arsenious sesquioxide, and by adding the nitric acid gradually, no application of artificial heat is necessary. No attempts to procure the dibasic and monobasic forms of arsenic acid have hitherto been successful; indeed the late Dr. Miller found that it formed but a single stable hydrate, the so-called *dihydrate*, $H_4As_2O_7$, or $As_2O_5.2OH_2$, and this was obtained whether the solution was evaporated over sulphuric acid at the ordinary temperature, or in the open air at any temperature not exceeding 150° (302° F.): in this way hard brilliant prisms of the dihydrate are formed; at a temperature of 260° (500° F.), these become anhydrous, and finally, if the mass be suddenly heated to redness, it fuses, and becomes decomposed into arsenious sesquioxide and oxygen.

If a current of sulphurous anhydride be passed through a solution of arsenic acid, it is slowly reduced to the state of arsenious acid, whilst sulphuric acid is formed, $H_3AsO_4+H_2SO_3$ becoming $H_3AsO_3+H_2SO_4$. Arsenic acid is now employed in calico-printing to some extent as a substitute for tartaric and phosphoric acids, but its employment is dangerous if the waste

products are allowed to run into the streams. Its chief consumption is in the preparation of magenta dye from aniline.

Arsenates.—Arsenic acid is a powerful tribasic acid, expelling the volatile acids from their combinations, and decomposing the carbonates with effervescence. The salts of this acid have the general formula, M'_3AsO_4, and of the 3 atoms of its basic hydrogen, 1, 2, or 3, may be replaced by a metal. It forms a series of soluble crystallizable salts with the alkali-metals, which present considerable interest, as they are isomorphous with the tribasic phosphates. Hydric disodic arsenate, the commercial *arsenate of soda*, is a manufactured product of considerable importance. It is best obtained by saturating arsenious anhydride with crude soda-ash, and deflagrating the dry residue in a reverberatory furnace with a suitable proportion of sodic nitrate. By adding sodic hydrate in excess to arsenic acid and evaporating the solution, an efflorescent salt, $Na_3AsO_4.12OH_2$,* may be obtained, which crystallizes in prismatic needles. If to a hot solution of arsenic acid, sodic carbonate be added until effervescence ceases, the salt which is obtained on evaporation, $Na_2HAsO_4.12OH_2$, corresponds in form and composition to the rhombic hydric disodic phosphate, although more usually it crystallizes with $7OH_2$; and by adding to a solution of this compound a quantity of arsenic acid equal to that which it contains, a deliquescent salt, $NaH_2AsO_4.OH_2$, is formed, which crystallizes with difficulty. The corresponding potassic dihydric arsenate crystallizes in bold, brilliant, octahedral crystals, KH_2AsO_4: it is readily prepared by deflagrating equal parts of arsenious anhydride and nitre, then dissolving the residue in water, and allowing it to crystallize. All these salts may be rendered anhydrous by heat, but when redissolved, they recover their basic water. An ammonic magnesic arsenate, $NH_4MgAsO_4.6OH_2$, may be procured in the form of prismatic crystals isomorphous with those of the corresponding phosphate, by mixing a solution of magnesic sulphate containing an excess of ammonia with a neutral or ammoniacal solution of an arsenate of one of the alkali-metals: it is sometimes used as a precipitant for arsenic acid; it is very sparingly soluble in weak ammoniacal solutions; when dried at 100° (212° F.), 2 molecules of the salt lose $11OH_2$, and the residue contains 60·52 parts of arsenic anhydride. A brick-red triargentic arsenate, Ag_3AsO_4, is pre-

* According to Fleury (*Jour. Pharm. Chim.*, [4], xxi. 395), it usually crystallizes with $7OH_2$.

cipitated when any arsenate in solution is mixed with a solution of argentic nitrate: it is readily soluble in excess either of nitric acid or of ammonia, and is characteristic as a test of arsenic acid. Hydric cupric arsenate, $CuHAsO_4$, is of a pale greenish-blue colour; the tricalcic and triplumbic diarsenates are white; whilst ferric and uranic salts give yellowish white arsenates: all these are readily soluble in excess of dilute nitric acid.

(993) **SULPHIDES OF ARSENIC.**—Arsenicum and sulphur may be melted together in all proportions; but they form several well-defined compounds: of these, the most important are realgar, As_2S_2; the sesquisulphide, or orpiment, As_2S_3; and the diarsenic pentasulphide, As_2S_5.

Realgar; $As_2S_2 = 214$; *Density*, 3·356.—This substance is occasionally found native in ruby-red prismatic crystals; it may be prepared artificially, by heating together 9 parts of arsenicum and 4 of sulphur; the ruby-red vitreous mass obtained by Berzelius's process of fusing a mixture of 198 parts of arsenious anhydride with 112 of sulphur; $2As_2O_3 + 7S = 2As_2S_2 + 3SO_2$ does not yield realgar, the product always containing much more sulphur than is required by the formula As_2S_2 (Nilson, *Jour. pr. Chem.*, 1875, [2], xii. 295). When heated in closed vessels, realgar melts, and at a higher temperature it sublimes without decomposition. The sublimed mass is hard, brittle, transparent, and of a beautiful red colour: if the realgar is contaminated with even a small quantity of arsenious anhydride, it is uncrystallizable, but if quite pure, it gradually assumes the crystalline state when heated for several hours. Realgar is insoluble in water: it is readily attacked by nitric acid and by aqua regia, but not by hydrochloric acid; potassic disulphide dissolves it and forms a double sulphide. Potassic hydrate decomposes it, leaving undissolved a black precipitate, consisting of metallic arsenic and a little sulphur, produced by a secondary action, $3As_2S_2 = 2As_2S_3 + As_2$. Realgar is one of the ingredients of *white Indian fire*, which is often used as a signal light: it is composed of a mixture of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

Arsenious Sesquisulphide, or *Orpiment*; $As_2S_3 = 246$; *Density*, 3·48; *Comp. in* 100 *parts*, As, 60·98; S. 39·02.—Orpiment (*auri pigmentum*, so called from its golden-yellow colour) is occasionally found native in crystals which have the same form as those of realgar—viz., the oblique rhombic prism: these crystals are flexible; they have a yellow colour, and a brilliant lustre. It may be prepared artificially by passing a current of sulphuretted hydrogen through a solution of arsenious acid, or of any of the arsenites, in hydrochloric acid; it then falls as a brilliant yellow amorphous powder. If the solution be very dilute, part of the sesquisulphide is retained in solution, forming a yellow liquid; by exposure to the air the excess of sulphuretted hydrogen is removed, and the sesquisulphide is gradually and completely deposited.

Orpiment is insoluble in water and in dilute acids, but it is decomposed by nitric acid and by aqua regia. It fuses easily,

and when heated in the air it burns with a pale blue flame; in closed vessels, however, it may be sublimed without undergoing decomposition. Ammonia and the fixed alkalies dissolve it, and form colourless solutions containing an alkaline arsenite and sulpharsenite. The ammoniacal solution is sometimes used for dyeing yellow, since by exposure to air the ammonia evaporates, leaving the yellow sesquisulphide firmly adherent to the fibre. The *sulpharsenites* may be prepared by dissolving orpiment in the respective sulphhydrates: they are mostly amorphous bodies. Orpiment is also soluble in solution of ammonic sesquicarbonate. This sesquisulphide is a feeble sulphur-acid, so that ammonic sulphide and the sulphides of the alkali-metals in solution dissolve it easily, and form double sulphides, which are decomposed on the addition of an acid. Orpiment is the colouring ingredient in the pigment called *King's yellow*, which is a mixture of arsenious sesquioxide with this sulphide.

Diarsenic Pentasulphide, $As_2S_5 = 310$, (*Comp. in 100 parts*, As, 48·39; S, 51·61) corresponds in composition to arsenic anhydride. When a stream of sulphuretted hydrogen is passed through a solution of arsenic acid, a yellow precipitate resembling orpiment in appearance, and consisting of a mixture of orpiment and sulphur, is very gradually separated (Rose). But by decomposing a dilute aqueous solution of the sulpho-salt, Na_3AsS_4, by the addition of an acid, a bright yellow precipitate of $As_2S_5.3SH_2$ is obtained, which, by prolonged boiling of the solution, loses the hydrogen sulphide, and is converted into arsenic pentasulphide, As_2S_5. Upon the application of heat, this sulphide fuses into a dark liquid, and forms a reddish-yellow glassy substance as it cools; it may be sublimed in closed vessels. It is soluble in alkaline hydrates, decomposes the carbonates with effervescence if boiled with their solutions, and forms crystallizable compounds with the sulphides of the metals of the alkalies and alkaline earths. The *trisodic sulpharsenate*, $2Na_3AsS_4.15OH_2$, may be prepared by saturating a solution of 10 parts of soda (reckoned as Na_2O) with sulphuretted hydrogen, adding an equal quantity of soda, and then dissolving 26 parts of orpiment and 7 of sulphur in the liquid by the aid of heat: on evaporation, the sodium-salt is obtained in pale yellow crystals. The sulphur-salt of potassium, $2K_2S.As_2S_5$, may be made by passing sulphuretted hydrogen through the solution of the hydric potassic arsenate. When an aqueous solution of this sulphur-salt of arsenic is mixed with alcohol, it undergoes decomposition, and by evaporating the alcoholic solution, after separating the insoluble portion by filtration, a still higher sulphide, AsS_9, was obtained by Berzelius in brilliant, yellow, crystalline scales.

Arsenic Phosphide, PAs.—This compound is obtained as a brown powder by the mutual decomposition of arseniuretted hydrogen and phosphorous trichloride. It is insoluble in alcohol, ether, and chloroform, but dissolves in a warm solution of potassic hydrate, with evolution of phosphoretted hydrogen and arseniuretted hydrogen, whilst phosphorous acid, arsenious acid, and metallic arsenic remain.

(994) **Characters of the Compounds of Arsenic.**—Arsenicum forms, with most of the metals, alloys which are generally brittle and easily fusible. The compounds of this metal are all highly

poisonous:* the substance which has the best claim to be considered as an antidote to it, is the freshly-precipitated hydrated ferric oxide, which should be suspended in water, and given freely, as soon as possible after the poison has been swallowed. It is only applicable when arsenic or arsenious acids have been taken uncombined with bases, as it forms an insoluble ferric arsenate; the arsenious acid being partially oxidized by the excess of hydrated sesquioxide, which is thereby reduced to the form of ferrous oxide. Calcined magnesia may be used if the ferric oxide be not at hand. In cases of arsenical poisoning, putrefaction of the body after death is retarded in a remarkable degree; indeed, in various instances where the body has been disinterred several months after death, it has been found to have been sufficiently preserved from decay, to allow many of the principal viscera to be distinguished In these cases, it has not unfrequently happened that yellow patches of orpiment have been observed in various parts of the alimentary canal, although it has been ascertained that the poison had been swallowed in the form of white arsenic. These patches of orpiment are occasioned by the disengagement of sulphuretted hydrogen from the decomposition of the tissues, by which the arsenious sesquioxide becomes partially converted into the sesquisulphide.

Arsenic can be identified in quantities so minute, as to be inappreciable by the balance. In minerals which contain it, its presence is revealed by the peculiar garlic odour which it emits when a fragment is heated in the reducing flame with sodic carbonate on charcoal, *before the blowpipe*. The compounds of arsenic may be detected by passing through the solution, acidulated with hydrochloric acid, a stream of *sulphuretted hydrogen* for six hours; a yellow precipitate is thus produced, which must be further examined as follows: the liquid must be exposed to a temperature of about 40° (104° F.), in a shallow vessel for six hours, to allow the gas to escape, and the precipitate to subside completely; the clear liquid must be decanted, and the precipitate collected on a small filter. A few drops of ammonia will dissolve it, and on evaporating this solution in a watch-glass by means of a water-bath, the arsenious sesquisulphide will be left. This substance is then subjected to the process of *reduction*, by mixing it with three times its bulk of black

* For a singular statement respecting the arsenic eaters of Styria, the reader is referred to a paper by Mr. Heisch, in the *Pharmaceutical Journal* for May, 1860, p. 556

flux,* or with a mixture of 1 part of potassic cyanide and 3 parts of sodic carbonate, previously well dried, and introducing it into a glass tube of the diameter of a common quill, care being taken not to soil the sides of the tube. The mixture is heated strongly by the blowpipe, when the arsenicum sublimes and is condensed as a brilliant mirror-like ring of steel-grey lustre in the upper part of the tube. The reaction which occurs when black flux is used, may be represented as follows: $2As_2S_3 + 6K_2CO_3 + 6C = As_4 + 6K_2S + 6CO + 6CO_2$.

Cadmic sulphide gives a yellow precipitate with sulphuretted hydrogen, but it is insoluble in ammonia: stannic salts also give a yellow precipitate with sulphuretted hydrogen, but no metallic sublimate when they are submitted to the process of reduction.

In addition to the preceding tests, arsenious acid may be readily detected in a *neutral* solution by *ammonia-nitrate of silver*. This is prepared by adding ammonia to a solution of argentic nitrate in very slight excess, so as nearly, but not entirely, to redissolve the precipitate of argentic oxide which is at first formed; the clear liquid is decanted for use. On adding this reagent to a solution containing an arsenite, a yellow precipitate of triargentic arsenite is produced, which is freely soluble both in ammonia and in nitric acid. As, however, the tribasic phosphates give a yellow precipitate with ammonia-nitrate of silver, and this precipitate also is soluble both in nitric acid and ammonia, a second test should be tried—viz., the *ammonia-sulphate of copper*, which is prepared from a solution of cupric sulphate by the addition of ammonia, with the same precautions as those prescribed for the preparation of the silver test. In neutral solutions containing an arsenite, this copper test occasions a green precipitate consisting of hydric cupric arsenite: it is soluble both in ammonia and in acids. The arsenites of silver and copper are formed immediately that the tests are added; the sulphide of arsenic does not appear at first if the metal be present as arsenic acid, as the compounds of arsenic acid are decomposed by hydrosulphuric acid more slowly than those of any other metal which is precipitable by this reagent.

(995) **Detection of Arsenic in Organic Mixtures.**—In the greater number of cases, however, where the search for arsenic becomes important, it is mixed with articles of diet, with the contents of the stomach, or with other matters of organic origin,

* A mixture of potassic carbonate and charcoal obtained by deflagrating equal weights of cream of tartar and nitre in a red-hot earthen crucible.

which render preliminary measures needful in order to get rid of them. If the substance be in the liquid form, any sediment which it may contain must be examined for solid particles of undissolved arsenious anhydride, which are frequently found, and to which the preceding tests are readily applied. If any solid particles of arsenious anhydride be found, their reduction is easily effected by drawing off a tube to the thickness of a crowquill, sealing one end, dropping in the suspected fragment, adding a minute quantity of dried sodic carbonate, and then a few small fragments of charcoal: on ignition, the metal is sublimed, and may be recognised by the steel-grey ring which it forms in the cool portion of the tube.

If no solid particles of the anhydride be visible, the liquid is boiled and filtered, and divided into three portions, one of which is set aside in case of accident.

A second portion is submitted to *Reinsch's test;* it is for this purpose acidulated with about $\frac{1}{10}$ of its bulk of pure hydrochloric acid, and boiled with bright slips of pure electrotype copper foil for half an hour.* If any arsenical compound be present, a metallic deposit will be found on the surface of the foil, which according to Lippert, consists of an arsenide of copper, Cu_3As_2. The copper is then withdrawn from the liquid, washed, dried at 100° (212° F.), and introduced into a narrow glass tube (of about the diameter of a quill), which is then drawn out to a capillary neck, taking care not to heat the copper foil in this operation. The tube is shown in fig. 356. The foil and the portion of the tube which contains it, are then heated nearly to redness; the arsenic combines with oxygen derived from the air in the tube, and it condenses in beautiful, transparent octahedra of arsenious anhydride on the contracted cool part of the tube. A preliminary experiment must be first tried with the copper and hydrochloric acid alone, in order to ascertain their purity before employing them as tests. The presence of nitrates or of chlorates interferes with the application of Reinsch's test, as the copper foil becomes

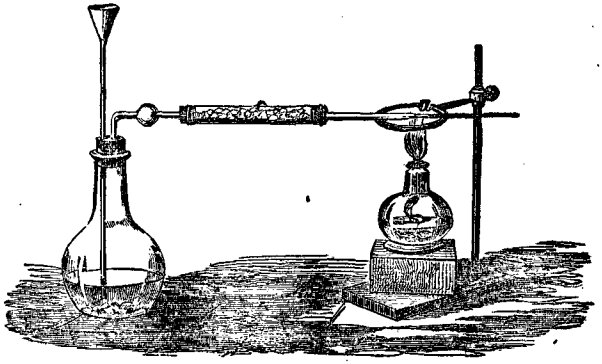
FIG. 356.

* Dilute solutions of arsenious acid in hydrochloric acid may be evaporated below 100° (212° F.), without loss of arsenious chloride, but if the mixture be distilled to dryness in a retort, the chloride passes over in the last portions, and may thus be separated from most other metals: the distillate may then be submitted to Reinsch's or Marsh's test. This furnishes an excellent method of procedure in many cases. See a paper by Dr. Taylor, in *Guy's Hosp. Reports*, vol. vi.

dissolved when boiled with the acidulated solution under these circumstances. If, however, the liquid be first acidulated with an excess of hydrochloric acid, and be evaporated by a gentle heat on a water-bath, the residue may be subjected to Reinsch's process as usual. A slip of metallic copper occasions precipitates in many metallic solutions when acidulated with hydrochloric acid and boiled with them; such, for example, as antimony, bismuth, tin, silver, mercury, lead, and cadmium, but cadmium is not precipitable from a strongly acid solution. Of these precipitates, mercury is the only one which, like arsenicum, is volatilized by heat in the metallic form, but the sublimate, when viewed with the microscope, is seen, if mercurial, to consist of globules, and is thus easily distinguished from arsenic. Moreover, the arsenical crust by resublimation is converted into arsenious anhydride, whilst no such change takes place with mercury. Antimony becomes oxidized, and sublimes with difficulty in needles, not in octahedra, and may be identified in the manner described at p. 755.

The third portion of the liquid is subjected to *Marsh's test*: the application of this test depends upon the formation of arseniuretted hydrogen, and the subsequent deposition of arsenicum from it by application of heat:—A wide-mouthed flask, fig. 357, of about 6 oz. (170 c. c.) capacity, is charged with a little pure

FIG. 357.



granulated zinc, or with fragments of magnesium; through the cork a tube funnel is passed to within an inch of the bottom; a bulb tube, bent to a right angle, passes just through the cork; the outer horizontal tube *c*, being loosely filled with calcic chloride to arrest any particles of fluid which might be carried up by the effervescence; it is prolonged by fitting into it

with a cork, a piece of German tube, *a*, free from lead and drawn out to a capillary termination. Some distilled water is next introduced by the funnel, and a little pure sulphuric acid added to cause a steady evolution of hydrogen. When all the atmospheric air is expelled, the flame of a spirit-lamp is placed under the point where the capillary contraction commences: if after ten minutes, the temperature of the glass being at a red heat, no indications of any metallic deposit show themselves, the materials used are sufficiently pure. Whilst the heat is still maintained, the suspected liquid is to be poured through the funnel into the bottle; if a compound of arsenic be present, it is reduced, and part of the arsenic combines with the nascent hydrogen, arseniuretted hydrogen is formed, and the gas is decomposed as it passes through the heated tube, the metal being deposited in the form of a steel-grey ring just beyond the spot where the heat is applied. If, instead of heating the capillary tube, the gas be kindled as it escapes, it will be found to burn with the peculiar flame of arsenic if the quantity present be at all considerable, and if a piece of cold white porcelain, such as a crucible lid, be introduced into the flame, the more combustible hydrogen is burned, and brown or grey mirror-like spots of reduced arsenic may be obtained upon the cold plate.* Tartar-emetic, if present, would, however, produce antimoniuretted hydrogen, which, by its decomposition, would give rise to appearances in the tube and on the porcelain resembling those of arsenicum. Fleitmann has shown that if the hydrogen be generated by dropping zinc into a strong boiling solution of potassic or sodic hydrate, and then adding the suspected arsenical liquid, the hydrogen which is given off contains the arsenic if this metal be present, but does not form antimoniuretted hydrogen with an antimonial compound. The antimonial spots also immediately disappear when a drop of ammonic sulphide, in which a little sulphur is dissolved, is added, and the solution, by its spontaneous evaporation, leaves the orange-coloured antimonious sesquisulphide; but the arsenical crusts are scarcely acted on by the ammonic sulphide (Dr. Guy). The chief practical difficulty in the use of Marsh's test, arises from the inconvenient way in which liquids containing organic matter frequently froth up during the operation. The best method of preventing this consists in first heating

* According to Blondlot the presence of minute quantities of nitric acid prevents the formation of the gaseous arseniuretted hydrogen, and causes the deposition of arsenic upon the zinc.

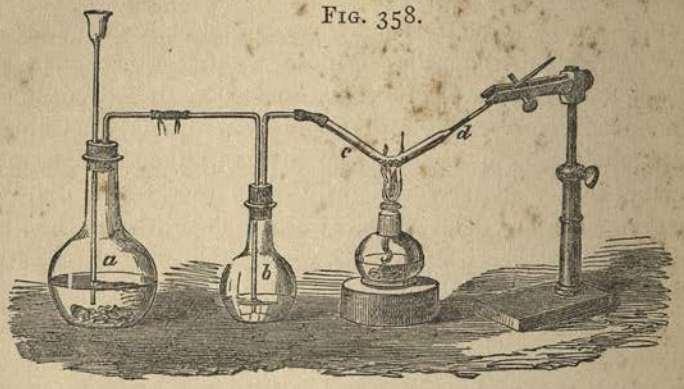
the suspected liquid with about a tenth of its bulk of hydrochloric acid, and adding a small quantity of potassic chlorate: the organic matter is thus destroyed, and after the liquid has become cool, it may be safely added to the zinc and sulphuric acid in the apparatus.

The process by sulphuretted hydrogen and subsequent reduction is extremely delicate, and open to no objection except the length of time required. Marsh's test is one of extraordinary delicacy, and the results are easily and quickly attained: Reinsch's test is also easy of application, and is extremely delicate; but they all act very slowly when the arsenic is in the form of arsenic acid. The arsenical crusts deposited in the glass tube are readily sublimed by a gentle heat, and may be converted into arsenious anhydride which forms minute brilliant octahedral crystals, and these again may be subjected to the test of the ammonia-nitrate of silver.

Although it may not be possible to detect arsenic in the fluids submitted to examination, it not unfrequently happens that the coats of the stomach, and sometimes the liver, will yet contain the poison in sufficient quantity to render its identification practicable. The best mode of proceeding in this case consists in cutting up the organ into shreds, heating it on a water-bath with a fourth of its weight of hydrochloric acid, the mixture being diluted with water until it becomes of the consistence of a thin paste. It may then be subjected to Reinsch's process, or it is fit for trial in Marsh's apparatus. Fresenius and Von Babo (*Ann. Chem. Pharm.*, 1844, xlix. 287) prefer to add to the original mixture of hydrochloric acid and organic matter, small portions of potassic chlorate from time to time until a homogeneous yellow liquid is obtained; when cold this is filtered through linen, the residue well washed, and the clear liquid is concentrated by evaporation by a heat not exceeding that of the water-bath. In this case it is necessary subsequently to reduce the arsenic acid in the liquid to arsenious acid by means of a current of sulphurous acid gas. Then heat gently to expel the excess of sulphurous acid, precipitate the arsenic by sulphuretted hydrogen, collect the precipitate on a small filter, wash, dissolve out the arsenious sesquisulphide with ammonia, evaporate the solution on a watch-glass, and reduce the sulphide by mixing it with about 12 times its weight of a mixture of 3 parts of dried sodic carbonate and 1 of potassic cyanide, and heating it in a very slow current of dried carbonic anhydride, as shown in fig. 358, in which *a* represents a flask containing fragments of marble from which the

carbonic anhydride is disengaged by the action of hydrochloric acid: *b* contains oil of vitriol in order to dry the issuing gas; the arsenical mixture is placed in the bend of the tube *c*, and the metallic crust is sublimed into the contracted part of the tube

FIG. 358.



at *d*. This process is tedious and complicated, and not superior to Reinsch's, if the latter be conducted with due care. A very delicate mode of detecting the presence of arsenic is afforded by the action of the voltaic current, which may be applied without difficulty by adopting the precautions recommended by Bloxam (*Jour. Chem. Soc.*, 1860, xiii. 12). The galvanic process has the advantage of being applicable to the detection of various other metallic poisons if arsenic be absent, as nothing is introduced which interferes with their subsequent identification by appropriate tests.

(996) **Estimation of Arsenic.**—It is not easy to determine accurately the quantity of arsenic present in a compound; but the following is the plan generally adopted:—The metal is precipitated in the form of a sulphide; the precipitate collected on a weighed filter, dried at 100° (212° F.) and weighed: a given weight of the sulphide is then oxidized by means of nitric acid (density 1·51); and when it is completely dissolved, the sulphur is precipitated as baric sulphate. From the weight of this precipitate the quantity of sulphur is calculated, and deducted from the total amount of arsenical sulphide; the difference gives the amount of the metal. This precaution is necessary, as the sulphide is apt to contain a variable quantity of free sulphur. Before it can be adopted, the absence of all other metals in the sulphide must, of course, be ascertained. The arsenic acid in the solution may further be precipitated as ammonic magnesic arsenate, by neutralizing with ammonia, and adding a solution of magnesic sulphate containing ammonic chloride and ammonia in excess: 100 parts of this precipitate, $2NH_4MgAsO_4.OH_2$, dried at 100° (212° F.), represent 39·47 of metallic arsenic.

(997) **Separation of Arsenicum from other Metals.**—By means of sulphuretted hydrogen and the subsequent solution of the sulphide in ammonic sulphide, arsenic is easily separated from all the foregoing metals with the exception of those which form soluble compounds with the sulphides of the alkali-

metals. A solution of ammonic sesquicarbonate (free from uncombined ammonia), when digested with the mixed hydrated arsenical and antimonial sulphides, dissolves the arsenical sulphide only, and leaves it on evaporation.

§ X. ANTIMONY: Sb‴ = 122.

(998) **ANTIMONY** (Stibium); *Density, 6·7 to 6·86; Fusing-pt.* 450° (842° F.); *Triad, as in* $SbCl_3$; *sometimes Pentad, as in* $SbCl_5$.—This metal, which is tolerably abundant, is always extracted from its sesquisulphide, although it is frequently found alloyed with other metals, and is sometimes met with in the native state.

Antimonious sulphide usually occurs in a matrix of quartz, baric sulphate, and limestone. The *crude antimony* of commerce is merely this sesquisulphide freed from the greater part of its earthy impurities. This is effected by placing the ore upon the bed of a reverberatory furnace covered with charcoal powder, the sulphide melts, the earthy impurities float, and the fluid portion is drawn off into an iron basin, and is afterwards cast into loaves or cakes. If it be desired to extract the metal, the sulphide thus purified is reduced to a coarse powder, and again placed upon the bed of a reverberatory furnace: the temperature may be gradually raised to dull redness, but must be moderated to prevent the mass from entering into fusion: in about 12 hours fumes cease to rise, most of the sulphur is expelled, and a red mixture of antimonious sesquioxide and sesquisulphide remains. During this process copious vapours of sulphurous and arsenious anhydrides are given off, accompanied by a considerable portion of antimonious oxide. It is stated that nearly 20 per cent. of the metal is lost during this operation. The roasted mass is now mixed with about one-sixth of its weight of powdered charcoal, made into a paste with a strong solution of sodic carbonate, and heated in crucibles to bright redness, when the metal collects at the bottom; the reactions are illustrated by the following equations: $Sb_2S_3 + 3Na_2CO_3 = 3CO_2 + 3Na_2S + Sb_2O_3$, and $Sb_2O_3 + 3C = Sb_2 + 3CO$; above it is a scoria, consisting chiefly of antimonic sodic sulphide. This scoria is known in the arts as the *crocus of antimony*. The metal is remelted with the scoria, and is then fit for sale, although it is not pure. 100 parts of sesquisulphide yield about 44 parts of metallic antimony, so that in the whole process about three-sevenths of the antimony are lost.

On the small scale the metal is most easily procured by taking 4 parts of the powdered sesquisulphide, 3 of crude tartar, and 1½ of nitre, mixing them

intimately, and throwing the powder in small portions at a time into a crucible kept at a bright red heat. The quantity of nitre employed is insufficient to oxidize both the sulphur and the metal; and the sulphur being the more combustible element of the two is the first to undergo oxidation, whilst the metal melts and collects at the bottom, beneath the slag of potassic sulphate. Commercial antimony commonly contains arsenicum, iron, and often small quantities of copper and lead.

In order to obtain antimony free from arsenic, Wöhler mixes intimately 4 parts of finely-powdered commercial antimony with 5 of sodic nitrate, and 2 of anhydrous sodic carbonate. The mixture is heated to redness in a Hessian crucible, and the antimony burns quietly at the expense of the oxygen of the nitrate. After the deflagration is complete, the crucible is covered, and the mass is kept for half an hour at a temperature sufficient to soften but not to fuse it, pressing it down from time to time with an iron spatula. It is removed from the crucible by means of a spatula, while still in a pasty condition, then pulverized and thrown into boiling water: the solution contains the sodic arseniate, while the greater part of the sodic antimoniate remains undissolved, and is well washed with boiling water. From this sodic antimoniate the metal is extracted by fusing it with half its weight of crude tartar. The product so obtained is an alloy of antimony with potassium: it is broken into small pieces and thrown into water; a copious disengagement of hydrogen takes place, the potassium is oxidized and dissolved, and the alloy falls to powder. It still retains iron, and sometimes lead. One-third of the mass is converted into oxide by means of nitric acid; this oxide is well washed with water, dried, and then incorporated with the powdered metal; the mass is again melted in a covered crucible, and pure antimony is obtained beneath a layer of fused sesquioxide, which retains the oxides of iron and lead.

(999) **Properties of Antimony.**—Antimony was well known to the alchemists. It is a brilliant, bluish-white metal, of a flaky, crystalline texture, and so brittle that it may readily be reduced to powder. It fuses at about 450° (842° F.), at a low red heat, and by slow cooling may be obtained in rhombohedral crystals, which, according to Mitscherlich, are isomorphous with those of arsenicum; absolutely pure antimony, however, crystallizes with difficulty (Cooke; Matthiessen). The commercial cakes of the metal exhibit upon their upper surface a beautiful stellate or fern-like crystalline structure. Melted antimony expands in solidifying, the solid metal floating on the melted portion. At a bright red heat it is volatilized slowly, the operation being facilitated by passing a current of hydrogen over it. Antimony is inferior to most of the metals as a conductor of heat and of electricity. When exposed to the air at ordinary temperatures, it undergoes no change, but if heated it burns brilliantly, emitting copious white fumes which consist chiefly of antimonious oxide. Powdered antimony takes fire spontaneously when thrown into chlorine gas; bromine and iodine likewise enter into combination with the metal with great evolution of heat, when they are brought into contact with it at ordinary temperatures. It is also

oxidized by nitric acid and by boiling sulphuric acid. Aqua regia dissolves it readily. When finely powdered and heated with strong hydrochloric acid, it is dissolved with evolution of hydrogen. Metallic antimony, in a finely-divided state, is readily dissolved by digestion with a solution of one of the higher sulphides of potassium, whilst the lead, iron, copper, bismuth, or silver which it may contain is left undissolved. If arsenicum or tin be present, small quantities of these metals enter into solution with the antimony.

(1000) **Alloys of Antimony.**—Antimony is not used alone in the arts, but it enters into the composition of several valuable alloys. *Type metal* is one of these: ordinary type is composed of 3 or 4 parts of lead, and 1 part of antimony: but the alloy which is now employed in the best description of type contains 2 parts of lead, 1 of tin, and 1 of antimony. Music type contains tin; and the common white metal used for teapots, under the name of *Britannia metal,* is an alloy of equal parts of brass, tin, antimony, and bismuth; another variety consists of 9 parts of tin and 1 of antimony. The value of the antimony in these alloys depends upon the hardness which it communicates to them, without rendering them inconveniently brittle, and to the property which it confers upon them of expanding in the act of solidification, so valuable in the case of type metal. Equal parts of antimony and lead, however, produce a brittle alloy. The compounds of antimony with zinc and tin are hard, white, and brittle. A mixture of 12 parts of tin, 1 of antimony, and a small quantity of copper, furnishes a ductile alloy, forming a superior kind of pewter. If lead be substituted for copper in this alloy it is rendered brittle. Antimony also combines readily with copper, furnishing a hard alloy which takes a good polish, but which becomes paler and more brittle in proportion as the quantity of antimony is increased. If 7 parts of powdered antimony and 3 of iron filings be exposed in a covered crucible to a very high temperature, a brittle alloy is formed which emits sparks when it is filed.

Antimony unites with zinc to form two definite alloys; these may be prepared by fusing the two metals together in the proper proportions, and can be obtained in the crystalline state by fusion in a manner similar to that adopted in the case of sulphur (413). One of these, Sb_2Zn_3, crystallizes in long acicular prisms, which belong to the oblique prismatic system; it decomposes water rapidly at 100° (212° F.) with evolution of hydrogen. The other alloy, SbZn, crystallizes in broad plates which twin together on an octahedral face.

Prof. J. P. Cooke, jun., who has studied these alloys minutely, finds that in such case, the crystalline form of the alloy is preserved, although the proportions of the two metals may vary within considerable limits; thus, the form of needles (which would require, if in atomic proportion, Sb_2Zn_3, a per-centage of

55·7 of antimony), is still preserved, although the antimony may fall as low as 35·77 or may rise as high as 57·24; while the form of plates is observed without any variation in the angular measurements, although the quantity of antimony may fall as low as 64·57 or may rise as high as 79·42 (65·07 would represent the true atomic proportion, SbZn). It is true both the forms belong to the same crystalline system, but they do not appear to be derivable one from the other. Prof. Cooke suggests that these observations may throw an important light upon the cause of the hitherto unexplained variation in composition occasionally observed in minerals of the same crystalline form, the components of which are not isomorphous; and he proposes the term *Allomerism* to designate such variation in the proportions of the constituents of the crystalline compound without any essential change in the crystalline form, the varying constituents not being isomorphous with each other.

Matthiessen and Von Bose, in their researches upon the alloys of tin and gold, have found that those containing from 27·4 to 43 per cent. of gold all crystallize in the same form, the largest and best defined crystals containing about 41 per cent. of gold ($AuSn_2$ = 45·9 per cent. of gold).

Antimonious oxide treated with hydric potassic tartrate produces tartar-emetic, a powerful and valuable medicine. The oxide, when ground up with linseed oil, furnishes a pigment which is employed to some extent as a substitute for white lead: it is much less injurious to the health of those who use it than pigments which contain lead.

Gore (*Phil. Trans.*, 1858, p. 185) has described a remarkable substance obtained by the electrolysis of a solution of antimonious trichloride in hydrochloric acid in the following manner:—Dissolve 1 part of tartar-emetic in 4 parts of the solution obtained by dissolving antimonious sulphide nearly to saturation in hydrochloric acid, and subject the solution to the action of two or three cells of Smee's battery, using a plate of antimony for the positive and copper wire for the negative electrode. A metallic deposit having the colour and lustre of highly-polished steel, with a peculiar mammellated surface and an amorphous structure, is formed. Its density is 5·8. The metal thus deposited retains 5 or 6 per cent. of antimonious chloride, and if struck sharply, or heated to about 80° (176° F.), or even scratched with a metallic point, it undergoes a rapid molecular change attended with a rise of temperature amounting sometimes to 250° (482° F.), accompanied by the disengagement of abundant fumes of antimonious chloride. The heat evolved is sufficient to boil water, or even to fuse small pieces of tin. After this change has occurred, the metal is found to retain its cohesion and its metallic aspect, but it has become grey, and acquired a granular fracture and an increased density. A corresponding substance may be obtained if antimonious bromide or iodide be submitted in electrolysis for the trichloride, the deposited metal in this case retaining a portion of the tribromide or tri-iodide: according to Böttger (*Chem. Centr.*, 1875, 674), it also contains occluded hydrogen.

(1001) **ANTIMONIURETTED HYDROGEN or STIBINE**; SbH_3?—The composition of this gas is not known with certainty, for it has never yet been obtained free from hydrogen. It is inferred, however, to contain 3 atoms of hydrogen to 1 atom of the metal, because, when passed through a solution of argentic nitrate, a precipitate of triargentic antimonide, $SbAg_3$, is formed; $3AgNO_3$ +

SbH_3 becoming $3HNO_3 + SbAg_3$. Antimoniuretted hydrogen mixed with a large quantity of free hydrogen is formed by dissolving an alloy of zinc and antimony in dilute sulphuric acid; a gas containing a much larger proportion of stibine is obtained by decomposing a concentrated solution of antimonious chloride with sodium amalgam. When a solution of any antimonious salt is poured into a mixture of zinc and sulphuric acid which is disengaging hydrogen, the antimonial salt becomes decomposed; one portion of the antimony is deposited in the form of a black powder upon the surface of the zinc, whilst another portion combines with the hydrogen, and assumes the gaseous state. It is most conveniently prepared, however (F. Jones, *Jour. Chem. Soc.*, 1876, i. 641), by allowing a concentrated solution of antimony in hydrochloric acid to drop on a considerable bulk of granulated zinc or zinc powder. The gas obtained in this way after being washed with a very dilute solution of sodic hydrate and dried over phosphoric anhydride, still contains a large excess of free hydrogen, but is nevertheless so strong that it often partly decomposes, depositing metallic antimony on the sides of the glass vessel containing it. It forms a colourless gas which has a distinct nauseating odour and an intensely disagreeable taste: it appears to be poisonous. When burned, it deposits white fumes of antimonious oxide, and if passed through a glass tube, heated to low redness, the gas is decomposed, and the antimony forms a brilliant metallic crust upon the heated portion of the tube. Stibine acts strongly on sulphur, forming antimonious sulphide and hydrogen sulphide: $2SbH_3 + 6S = Sb_2S_3 + 3SH_2$.

(1002) **ANTIMONIOUS CHLORIDE**, or *Trichloride of antimony*; $SbCl_3 = 228{\cdot}5$; *Density of Liquid at* 73° (163°·4 F.), 2·676; *of Vapour, Theoretic*, 7·906; *Observed*, 7·8; *Fusing-pt.* 72° (161°·6 F.); *Mol. Vol.* [ ]; *Rel. wt.* 114·25; *Boiling-pt.* 223° (433°·4 F.); *Comp. in* 100 *parts*, Sb, 53·39; Cl, 46·61.—Antimony has a powerful attraction for chlorine, and forms two chlorides, $SbCl_3$ and $SbCl_5$, the former of which, from its ready fusibility, was formerly known under the name of *butter of antimony*. It may be obtained in the anhydrous form by distilling an intimate mixture of 8 parts of corrosive sublimate with 3 of powdered metallic antimony; calomel, antimonious trichloride, and an amalgam of antimony are formed; $Sb_4 + 4HgCl_2 = 2SbCl_3 + Sb_2Hg_2 + Hg_2Cl_2$. Antimonious chloride may be more cheaply prepared by mixing antimonious sulphate with twice its weight of sodic chloride, and then distilling the mixture, or by passing chlorine over metallic antimony, taking care to keep the latter

in excess. On distilling the product, the trichloride is obtained as a volatile, fusible, crystallizable compound, which is deliquescent, and powerfully corrosive in its action on animal tissues. It may also be obtained by distilling the residue left on dissolving antimonious sulphide in hydrochloric acid. Antimonious chloride is soluble in hydrochloric acid, and in a small quantity of water; but if thrown into a large mass of water an insoluble oxychloride, SbOCl or $SbCl_3.Sb_2O_3$, falls, which gradually assumes a compact crystalline form; it was formerly called *powder of algaroth*. On diluting a hot solution of antimonious chloride in hydrochloric acid with hot water, it deposits, on cooling, brilliant needles, which may be represented as $2SbCl_3.5Sb_2O_3$. By heat, the trichloride is sublimed, leaving the sesquioxide. Antimonious chloride is used for bronzing gun-barrels, in order to prevent them from rusting.

(1003) **ANTIMONIC CHLORIDE**, or *Pentachloride*, $SbCl_5 = 299{\cdot}5$, is prepared by exposing pure antimonious chloride, gently heated in a retort, to a current of dry chlorine in excess. It forms a volatile, colourless or yellowish liquid, which emits dense, suffocating white fumes when exposed to the air, but it cannot be distilled without decomposition. At a low temperature it solidifies to a mass of needles which melt at $-6°$ ($21°{\cdot}2$ F.). With a small quantity of water it forms white, deliquescent crystals, which from the researches of Daubraiva (*Ann. Chem. Pharm.*, 1877, clxxxvi. 110) would appear to be an oxychloride, $SbOCl_3$, analogous to phosphoric oxychloride; this is decomposed by a large quantity of water, and metantimonic acid, which retains a little hydrochloric acid, is deposited: $2SbCl_5 + 7OH_2 = H_4Sb_2O_7 + 10HCl$. Dry antimonic chloride absorbs sulphuretted hydrogen, and forms with it a white, crystalline, fusible solid, $SbCl_5S$, which corresponds in composition to phosphoric chlorosulphide; it also forms definite compounds with the higher chlorides of phosphorus, sulphur, and selenium. Both the antimony chlorides form definite compounds with ammonia. The pentachloride is sometimes used as a chlorinating agent, since it readily parts with a portion of its chlorine to many compounds of organic origin which contain hydrogen.

(1004) **ANTIMONIOUS BROMIDE**, $SbBr_3$, or the *Tribromide*, is a colourless, crystalline solid which may easily be obtained by the action of a solution of bromine in carbonic bisulphide on metallic antimony. It is left on evaporation of the solvent in rhombic pyramids.

Antimonious Iodide, SbI_3, may be obtained in a similar manner to the bromide, or by heating a mixture of antimonious sulphide and iodine. It forms large red hexagonal plates, which melt at $164°{\cdot}4$ ($328°$ F.), and are soluble in carbonic bisulphide. It forms beautifully crystalline double salts with the alkaline iodides. *Antimonic iodide*, SbI_5, is said to be formed by heating a mixture of antimony and iodine in the right proportions, but its existence is somewhat doubtful.

ANTIMONIOUS FLUORIDE, SbF_3, is obtained in rhombic octahedra on evaporating a solution of antimonious oxide in hydrofluoric acid. It is deliquescent and easily soluble in water: like the iodide, it forms double salts with the alkaline fluorides. *Antimonic fluoride*, SbF_5, is obtained as a gummy

mass on evaporating a solution of antimonic oxide in hydrofluoric acid in a vacuum: it forms crystalline compounds, however, with the alkaline fluorides.

(1005) **OXIDES OF ANTIMONY.**—Antimony forms three well-marked oxides: the first is the most important, as it constitutes the basis of the antimonial salts employed in medicine. The oxides have the following composition:

			Oxygen.	Antimony.
Antimonious oxide	...	Sb_2O_3	= 16·44	+ 83·56
Antimonic anhydride	...	Sb_2O_5	= 24·69	+ 75·31
Antimonious antimoniate	...	$Sb_2O_3.Sb_2O_5$	= 20·78	+ 79·22

(1006) **ANTIMONIOUS OXIDE,** or *Sesquioxide of antimony,* formerly called the *teroxide;* $Sb_2O_3 = 292$.—In the anhydrous state this oxide is found crystallized in prisms in a somewhat rare mineral called *white antimony ore,* of density 5·56. The anhydrous sesquioxide is easily prepared from powdered metallic antimony by boiling to dryness in an iron ladle, with excess of strong sulphuric acid; an insoluble sulphate is formed, and sulphurous anhydride is disengaged. To remove the sulphuric acid, the residue is treated with sodic carbonate and well washed: the greyish-white insoluble powder which remains is the sesquioxide. When heated it assumes a yellow colour, but recovers its whiteness on cooling. When heated in closed vessels it may be melted; it is volatile at a high temperature, and the vapour condenses in brilliant crystalline needles isomorphous with the unusual form of arsenious anhydride. Occasionally it crystallizes in octahedra, like the common variety of arsenious anhydride. In the open air it burns like tinder, and is converted into the so-called antimonious acid. Hydrochloric and tartaric acids dissolve it freely. Nitric acid converts it into one of the higher oxides of antimony. Although its basic properties are but feeble, it unites with sulphuric acid to form an insoluble sulphate, Sb_23SO_4: this salt may be obtained in long silky needles by evaporating a solution of antimonious oxide in moderately concentrated sulphuric acid. The hydrated oxide may be obtained by pouring a solution of antimonious chloride into an excess of a solution of sodic carbonate. In this form it is readily soluble in solutions of potassic or sodic hydrates; but the simple ebullition or evaporation of the liquid causes a separation of antimonious oxide in prismatic crystals.

(1007) **ANTIMONIC ANHYDRIDE,** formerly *Antimonic acid;* $Sb_2O_5 = 324$.—This compound may be obtained by oxidizing the metal with nitric acid, and expelling the excess of nitric acid by a heat below redness. It is of a pale yellow colour, is tasteless, and insoluble in water. A strong heat

expels one-fifth of its oxygen, and converts it into antimonious antimoniate, Sb_2O_4, which is a white powder, formerly termed *antimonious acid*, but which possesses no acid characters; for if treated with hydric potassic tartrate (cream of tartar) it is decomposed, antimonious potassic tartrate (*tartar-emetic*) being formed, whilst antimonic anhydride is left; $2Sb_2O_4 = Sb_2O_3 + Sb_2O_5$.

(1008) **Antimoniates.**—Antimonic acid forms definite compounds with the metals of the alkalies: a boiling solution of potassic hydrate dissolves it, and on the addition of an acid, the liquid deposits hydrated antimonic acid in the form of a white powder, $Sb_2O_5.4OH_2$, which reddens litmus, and is freely soluble in cold solutions of the alkalies, and in hydrochloric acid. Fremy states that antimonic acid may, like hydrated stannic dioxide, be obtained in two modifications, each of which combines with different amounts of base, and forms a distinct class of salts: to one of these modifications, obtained by treating metallic antimony with nitric acid, he gives the name of *antimonic acid;* its normal potassic salt has the formula $K_2Sb_2O_6.5OH_2$, or $K_2O.Sb_2O_5.5OH_2$, or $2KSbO_3.5OH_2$: the other modification formed on decomposing antimonic pentachloride with water, he terms *metantimonic acid.* To the normal potassic salt of the latter acid he assigns the composition indicated by the formula, $2K_2O.Sb_2O_5$, or $K_4Sb_2O_5$.

According to Fremy, antimonic acid is monobasic, but it is capable of forming both normal and acid salts. The normal antimoniates are gelatinous and uncrystallizable. *Normal potassic antimoniate* may be prepared by heating 1 part of metallic antimony with 4 parts of nitre in an earthen crucible. The white mass so obtained is powdered, and washed with warm water to remove the excess of potash and potassic nitrite. The residue must be boiled in water for an hour or two; the *insoluble anhydrous* antimoniate is thus converted into a *soluble* hydrated modification consisting of $K_2Sb_2O_6.5OH_2$. The insoluble residue now consists chiefly of acid-antimoniate of potassium. The normal salt possesses the property of freely dissolving the acid-antimoniate, which is precipitated when such a solution is mixed with any neutral salt of one of the alkalies. The normal antimoniate does not crystallize, but forms a gummy mass which has an alkaline reaction; it is readily decomposed by acids, including carbonic, whilst the acid-antimoniate is deposited. When heated to 160° (320° F.) it loses 2 out of its 5 molecules of water, and becomes insoluble in cold water.

Acid-antimoniate of potassium, $K_2Sb_4O_{11}$, or *Dipotassic diantimoniate,* $K_2O.2Sb_2O_5$, is obtained by passing a current of carbonic anhydride through a solution of the normal antimoniate. It is quite insoluble in water, but is soluble in a hot solution of the normal antimoniate, and is deposited in crystals as the liquid cools.

If antimonic anhydride be heated with plumbic oxide it combines with it and yields a yellow compound, which is used as a pigment under the name of *Naples yellow.*

(1009) **METANTIMONIC ACID,** $H_4Sb_2O_7$, or $Sb_2O_5.2OH_2$.—This compound derives its principal interest from the circumstance of its yielding a soluble compound with potassium, which may be employed as a test for sodium. The metantimoniates of the alkalies are crystallizable. The *acid-metantimoniate of potassium,* $K_2H_2Sb_2O_7.6OH_2$, or *hydric potassic metantimoniate,* is the salt which is used for this purpose. In preparing this compound, potassic antimoniate is first formed by deflagrating antimony with nitre, washing and boiling the residue in the manner already described, so as to bring the whole of the normal

antimoniate into solution: the liquid thus obtained is filtered, and evaporated to a syrupy consistence in a silver dish; fragments of potassic hydrate are then added, and the evaporation is continued until a drop of the liquid placed upon a cold slip of glass begins to crystallize; it is then allowed to cool, and the alkaline supernatant liquid is poured off the crystals, which are allowed to drain upon a porous tile. When the salt is required as a test for salts of sodium, 30 or 40 grains (2 or 3 grams) of this residue are to be washed quickly with about twice their weight of cold water, and allowed to subside; this wishing is to be repeated two or three times, in order to remove traces of adhering potash; lastly, the residue should be digested with a little cold water for a few minutes, and the filtered liquid may then be used to ascertain the presence of sodium. The presence of potassic hydrate impairs the delicacy of the reaction. One great inconvenience which attends the use of this reagent is the circumstance, that if the solution be kept for a few days, the salt passes spontaneously into the normal antimoniate, and this salt does not precipitate the compounds of sodium; both salts contain exactly the same amount of acid and of base ($K_2H_2Sb_2O_7 = K_2Sb_2O_6.OH_2$), the difference in properties being due to difference in the molecular constitution of the two salts. If the solution of the acid metantimoniate be boiled, its conversion into normal antimoniate is effected in a few minutes. The *acid sodic metantimoniate*, $Na_2H_2Sb_2O_7.6OH_2$, is an insoluble salt, which crystallizes in octahedra.

(1010) **SULPHIDES OF ANTIMONY.**—Two compounds of antimony with sulphur are known; the ordinary sesquisulphide, Sb_2S_3, and the antimonic sulphide, Sb_2S_5, corresponding to the antimonious sesquioxide and to antimonic anhydride. They are usually regarded as sulphur acids, since they combine with the sulphides of the alkali-metals, and form definite salts.

(1011) **ANTIMONIOUS SULPHIDE,** or *Sesquisulphide of antimony,* $Sb_2S_3 = 340$; *Density,* 4·516 to 4·626; *Comp. in* 100 *parts,* Sb, 71·77; S, 28·23.—This substance constitutes the only ore from which the metal is obtained. The native sesquisulphide, or *grey antimony ore,* is usually found in granite or slate rocks, and generally contains lead and arsenic, besides a variable amount of pyrites. It occurs crystallized in four-sided prisms, striated transversely; it has a bluish-black colour, and a strong metallic lustre. It is friable, and melts below a red heat, crystallizing as it cools. It may be distilled unchanged in closed vessels, at a very high temperature, but by roasting in the open air it is converted into a fusible mixture of antimonious sesquioxide and sesquisulphide. This oxysulphide, after it has been fused, constitutes the commercial *glass of antimony,* which contains about 8 parts of the sesquioxide to 1 part of sesquisulphide. If the sesquioxide be in excess, the glass is transparent, and of a fine red colour: the greater the proportion of the sesquisulphide, the darker is the tint. The glass attacks the silica of the crucible in which the fusion is performed, and dissolves a considerable portion of it. A native *oxysulphide* of

antimony ($Sb_2O_3.2Sb_2S_3$, known as *red antimony ore*) occurs crystallized in oblique rhombic prisms.

Antimonious sulphide may be obtained in crystals by melting together, at a red heat, a mixture of sulphur and the sesquioxide: sulphurous anhydride escapes, and antimonious sulphide is formed: $2Sb_2O_3 + 9S$ becoming $2Sb_2S_3 + 3SO_2$.

Attempts have been recently made, with some success, to introduce the artificial sesquisulphide as a red pigment, under the name of *antimony vermilion*. The colour is prepared by pouring a crude solution of antimonious chloride in hydrochloric acid into a dilute solution of calcic thiosulphate (hyposulphite), which is maintained in excess; on heating the liquid to 60° (140° F.), it becomes turbid, and deposits a precipitate which is at first yellow but ultimately becomes a bright orange-red. The anhydrous sesquisulphide may also be obtained of a beautiful orange colour, by passing sulphuretted hydrogen through a solution of any salt of the metal: on being heated in closed vessels, it assumes a dark metallic appearance, resembling that of the native sulphide. If heated in a current of hydrogen, the sulphur is removed and metallic antimony is left. The sesquisulphide, whether artificial or native, is dissolved by hot concentrated hydrochloric acid, and furnishes a convenient source of pure sulphuretted hydrogen, provided that the gas be washed, to free it from traces of antimony and hydrochloric acid which it is apt to retain in suspension.

Antimonious sulphide is readily soluble in solutions of the sulphides of the alkali-metals, and forms colourless compounds, which have been regarded as double sulphides, or *sulphantimonites*; a hot solution of the alkaline sulphide can dissolve much more of the sesquisulphide than it can retain when cold; on the addition of an acid, the sulphide of the alkali-metal is decomposed, and the antimonious sulphide is reprecipitated. If the sesquisulphide in fine powder be boiled with a solution of potassic carbonate or hydrate, it is dissolved, and on cooling, the filtered liquid deposits a reddish-brown substance, known as *Kermes mineral*. This substance is not a definite compound, but is a variable mixture of antimonious sesquisulphide and sesquioxide, the latter being combined with a small portion of alkali. The action of potassic carbonate on the sesquisulphide may be represented as follows:

$$6K_2CO_3 + 3Sb_2S_3 + 3OH_2 = 6KHCO_3 + 3K_2S + 2Sb_2S_3.Sb_2O_3.$$

In this mixture of Sb_2S_3 and Sb_2O_3, H. Rose found crystals of antimonious oxide, which were visible by the aid of the microscope. Cream of tartar, or dilute hydrochloric acid, dissolves out the sesquioxide, leaving the sesquisulphide. If to the liquid, after deposition of the kermes, hydrochloric acid be added, effervescence takes place, with escape of sulphuretted hydrogen, owing to the decomposition of the dipotassic sulphide, the excess of antimonious sulphide which it retained being precipitated as the *golden sulphide of antimony*. This sulphide contains a larger proportion of sulphur than the sesquisulphide, from the gradual oxidation of the antimony in the solution before the precipitation is effected.

(1012) **ANTIMONIC SULPHIDE,** or *Sulphantimonic acid*, $Sb_2S_5 = 404$; *Comp. in* 100 *parts*, Sb, 60·4; S, 39·6.—This compound may be obtained by passing a current of sulphuretted hydrogen through an acid solution of antimonic pentachloride. It forms an orange-yellow precipitate which is anhydrous, but is remarkable for the facility with which it combines with the sulphides of the alkali-metals. The *trisodic sulphantimoniate*, $Na_3SbS_4.9OH_2$, or Schlippe's salt, crystallizes in large, and very brilliant, transparent tetrahedra.

It may be obtained in various ways: the easiest plan consists in thoroughly mixing 18 parts of finely-powdered antimonious sulphide, 12 of dried sodic carbonate, 13 of quicklime, and 3½ of sulphur; the mixture is ground up with water, and placed in a well-closed bottle, which is completely filled with water; it is allowed to digest, with frequent agitation, for 24 hours; the clear liquid is filtered off, and allowed to evaporate spontaneously in a closed vessel over sulphuric acid. This salt, when mixed with an acid, deposits pure antimonic sulphide. The moist crystals when exposed to the air absorb carbonic anhydride and become brown.

(1013) **Characters of the Compounds of Antimony.**—According to Péligot (*Ann. Chim. Phys.*, 1847, [3], xx. 297), antimonious oxide, by its reaction with acids, forms salts which contain 1, 2, or 4 equivalents of a monobasic acid radicle. Most of them when largely diluted with water become milky from the deposition of a basic salt of sparing solubility; but this milkiness disappears on the addition of tartaric acid, or of hydric potassic tartrate. The salts are all colourless, and when taken internally in large doses produce poisonous effects. Infusion of cinchona bark yields a copious insoluble precipitate with antimonial salts, and it has been recommended to administer this medicine in cases of poisoning with antimony: it is not, however, to be relied on.

Except when tartaric acid is present, the *alkaline hydrates* give, with antimonial salts, a white precipitate soluble in excess of the alkali; *ammonia* and the *carbonates of the alkalies*, a white precipitate nearly insoluble in excess. But the characteristic reaction of these salts when in solution is the formation of an orange-coloured precipitate of antimonious sulphide, when their solutions, acidulated with hydrochloric acid, are acted on by *sulphuretted hydrogen;* this precipitate is soluble in ammonic hydric sulphide. In detecting antimony for medico-legal purposes, antimoniuretted hydrogen is first prepared, and subsequently decomposed by heat. In order to effect this, the suspected liquid, after boiling with hydrochloric acid and a little potassic chlorate, is filtered and introduced into Marsh's apparatus; the experiment is then proceeded with as directed for arsenic (995). A more delicate method is the following:—The suspected solution is acidulated with hydrochloric acid, and boiled with a slip of bright copper foil, which becomes coated with a violet-coloured film of reduced antimony: when heated, with the precautions directed in applying Reinsch's test for arsenic (p. 741), the antimony gradually becomes oxidized, and at a high temperature the oxide is volatilized, condensing in needles, unlike those from arsenic, which are octahedra: but the

metal may be identified by heating the slip in a tube with a solution of pure potassic hydrate, exposing the surface of the metal freely to the air; the antimony is gradually oxidized and dissolved. The solution should next be somewhat diluted, submitted to the action of sulphuretted hydrogen, filtered from any sulphide of copper or lead, and then on the addition of hydrochloric acid in slight excess the antimony is precipitated as sesquisulphide in characteristic orange flocculi. This precipitate may be dissolved in hydrochloric acid, and will then give a crust of metallic antimony if introduced into Marsh's apparatus.

(1014) **Estimation of Antimony.**—In determining the quantity of this metal, the solution is first acidulated with a mixture of hydrochloric and tartaric acids; then subjected to a current of sulphuretted hydrogen, and exposed for a few hours in an open, shallow dish, at a temperature not exceeding 40° (104° F.): the excess of sulphuretted hydrogen is thus got rid of, and the whole of the antimony is separated as sesquisulphide, but the weight of the dried precipitated sesquisulphide cannot be relied upon as furnishing a correct datum for estimating the metal, because it is liable to contain a variable excess of uncombined sulphur. It must therefore be dried at 100° (212° F.), and weighed; a certain proportion of it is then dissolved in hot aqua regia, after which the solution is mixed with a little tartaric acid, and the sulphur, which by this means has been converted into sulphuric acid, is precipitated by the addition of baric chloride: the sulphur is calculated from the weight of the baric sulphate obtained, and deducted from the weight of antimonious sulphide employed; the difference is estimated as antimony. According to Bunsen, the sulphide may be converted into the so-called antimonious acid, Sb_2O_4, in which form it may be weighed, by proceeding as follows:—Place the sulphide in a counterpoised porcelain capsule, with a concave cover, moisten it with red concentrated nitric acid, and evaporate to dryness by the aid of a water bath: the white mass of antimonious sesquisulphate, which is left, is converted by ignition into antimonious acid, 100 parts of which correspond to 79·22 of the metal. The oxidation of the antimonial sulphide may also be effected by mixing it intimately with 40 or 50 times its weight of mercuric oxide, and simply igniting the mixture in a covered crucible until it ceases to lose weight; sulphurous anhydride and metallic mercury are expelled, and antimonious acid is left as before. If the precipitate contain a large excess of sulphur, it may be digested with carbonic bisulphide before proceeding to the oxidation. Antimony may be separated, by means of sulphuretted hydrogen, from all the metals previously described, with the exception of cadmium, tin, tungsten, molybdenum, and arsenicum. Cadmic sulphide is not soluble in ammonic hydric sulphide, whilst that of antimony is soluble; this liquid may therefore be employed to separate these metals.

(1015) **Separation of Antimony from Arsenic and Tin.**—In order to *separate arsenic from antimony*, the mixed sulphides are digested in a solution of ammonic sesquicarbonate containing no free ammonia: this solvent takes up the arsenious sulphide, but dissolves scarcely any antimonious sulphide.

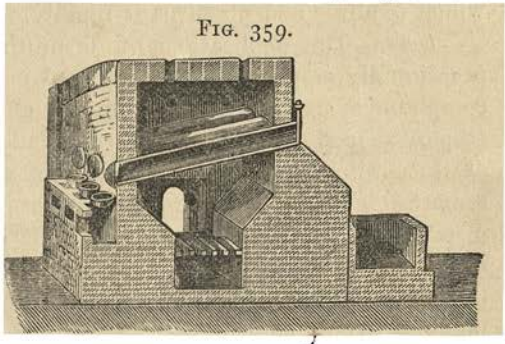
The *separation of antimony from tin* in a metallic alloy may be effected with tolerable accuracy, by dissolving the alloy in hydrochloric acid, which is to be mixed with a small proportion of nitric acid, in order to prevent loss of antimony as antimoniuretted hydrogen. The two metals are then precipitated together by means of metallic zinc, and the pulverulent metals are dried at 100° (212° F.) and

weighed. This precipitate is redissolved in weak aqua regia, and is digested at a gentle heat with a bar of tin, which throws down antimony only. The precipitated metal is collected, washed, dried, and weighed.

§ XI. BISMUTH: Bi″=210.

(1016) **BISMUTH**; *Density*, 9·83; *Fusing-pt.* 268°·3 (514°·9 F.); *Triad, as in* $Bi'''Cl_3$; *rarely Pentad, as in* $Bi^{v}_{2}O_5$.—This is not an abundant metal; it occurs generally in the native state in quartz rock, and is extracted from its matrix by simple fusion, the mineral being usually heated in iron tubes, which are placed across the furnace in an inclined position; the ore is introduced at the upper end, and the melted metal is drawn off into iron basins below, by opening a plugged aperture at intervals. Fig. 359 shows a section of the furnace used at Schneeberg in this operation, where the bismuth is extracted from an ore rich in cobalt. Occasionally it is found as a sesquioxide, or as a sesquisulphide, and sometimes it is met with combined with tellurium. It generally contains silver, which may be extracted by cupellation.

Fig. 359.



Its mines occur for the most part in Saxony, Transylvania, and Bohemia. Commercial bismuth is never pure: it is apt to contain a little sulphur and arsenic, which may be got rid of by fusing the metal with about one-tenth of its weight of nitre; but it still retains silver, lead, and iron. It may be obtained free from these impurities by solution in nitric acid: the acid liquid when saturated with the metal is allowed to become clear, and is then poured into a large bulk of water. A sparingly soluble basic bismuthous nitrate is thus precipitated; it is washed, dried, and reduced in a crucible by ignition with one-tenth of its weight of charcoal; pure bismuth collects at the bottom. Bismuth may also be purified, according to Türach (*Jour. pr. Chem.*, 1877, [2], xiv. 309), by fusing it under a layer of potassic chlorate containing a very little sodic carbonate; or by precipitating the slightly acid solution by oxalic acid, and igniting the precipitated bismuthous oxalate.

Properties.—Bismuth is a hard, brittle metal, of a reddish-

white colour; it fuses at 268°·3 (514°·9 F.), (264° according to Rudberg or 267° Person), and it expands considerably at the moment of congelation; by slowly cooling a fused mass of the pure metal (72), it may be obtained crystallized in large cubes,* which are frequently hollow. Marchand and Scheerer found that the density of bismuth was diminished by powerful compression, probably owing to the formation of minute internal fissures; they thus reduced it from 9·799 to 9·556. Bismuth is but very slightly volatile when strongly heated. It is but little altered by exposure to the air at ordinary temperatures, but is rapidly oxidized if exposed to the air at a red heat; if thrown in powder into chlorine it takes fire: it also unites easily with bromine, iodine, and sulphur. Hydrochloric acid has little action on it. Boiling sulphuric acid oxidizes it with evolution of sulphurous anhydride, but its proper solvent is nitric acid, which oxidizes and dissolves it rapidly.

Uses.—The applications of bismuth are but limited; it is occasionally employed instead of lead in cupellation; some of its compounds are used as pigments, and the basic nitrate is employed medicinally. Bismuth greatly increases the fusibility of those alloys into the composition of which it enters; the most remarkable being that known as *fusible metal*. This is composed of 2 parts of bismuth, 1 of lead, and 1 of tin, or 2 atoms of bismuth, 1 of lead, and 2 of tin. The mixture fuses at a little below 100° (212° F.), and passes through a pasty condition previous to complete fusion. It dilates in an anomalous manner when exposed to heat; according to Ermann it expands regularly from 0° to 35° (32°—95° F.), then contracts gradually to 55° (131° F.), at which point it occupies a less bulk than it did at 0° (32° F.); it then expands rapidly until it reaches 80° (176° F.), and from that point until it melts its expansion is uniform. This faculty of expanding as it cools, while still in the soft state, renders the alloy very valuable to the die-sinker, who employs it to test the perfection of his die,—every line being faithfully reproduced on taking a cast. The addition of cadmium to this alloy depresses its fusing-point still further (792).

(1017) **BISMŪTHOUS CHLORIDE,** or *Trichloride of bismuth*, $BiCl_3 = 316·5$; *Theoretic Density of vapour*, 10·9509; *Observed*, 11·16; *of solid*, 4·56; *Mol. Vol.* [illegible]; *Rel. wt.* 158·25.—This may be obtained by heating bismuth in an atmosphere of chlorine, or by mixing the metal in fine

* The crystals of bismuth, however, belong to the rhombohedral system, as they are not true cubes, but rhombohedra, the angles of which are within 2° 20′ of right angles.

powder with twice its weight of corrosive sublimate, and distilling. The crystals melt at 225°—230° (437°—446° F.), and may be distilled unchanged in a current of carbonic anhydride. When heated in a current of dry hydrogen the trichloride is converted into a black substance, possibly a lower chloride, Bi_2Cl_4, as when it is strongly heated, bismuthous trichloride sublimes and metallic bismuth is left. The trichloride is deliquescent, and is decomposed by a large quantity of water into free hydrochloric acid and bismuthous oxychloride, $2(BiCl_3.Bi_2O_3).OH_2$ or BiOCl, known under the name of *pearl white*. This compound is insoluble in tartaric acid, in solution of potassic hydrate, and in ammonic hydric sulphide, characters which distinguish it from the corresponding compound of antimony.

(1018) **BISMUTHOUS BROMIDE**, or *Tribromide of bismuth*, $BiBr_3 = 450$.—Bromine combines readily with metallic bismuth, forming a tribromide which may be obtained in flat, brilliant, golden-yellow crystals by sublimation at a gentle heat, but some oxybromide appears to be formed at the same time. It melts at 210°—215° (410°—419° F.), and is decomposed by water in a manner similar to the chloride yielding an oxybromide, BiOBr, as a white amorphous powder.

(1019) **BISMUTHOUS IODIDE**, or *Tri-iodide of bismuth*, $BiI_3 = 591$; *Density*, 5·652, is obtained by heating in closed vessels 6 parts of bismuth with 11 of iodine; it sublimes in six-sided, brilliant plates. It is of a dark-brown colour, readily fusible, and insoluble in water; but it forms soluble compounds with hydrochloric acid, and with potassic iodide.

(1020) **OXIDES OF BISMUTH.**—Bismuth forms two principal oxides: a sesquioxide, bismuthous oxide, Bi_2O_3, and an acid oxide or anhydride, Bi_2O_5; besides these there is a compound oxide, Bi_3O_4, formed by the union of the two preceding combinations. A lower oxide, Bi_2O_2, of a velvet-black colour, is formed by heating bismuth with free access of air a little above its melting point, and may also be obtained (Schneider) by treating equivalent quantities of bismuthous chloride and stannous chloride with an excess of potassic hydrate, filtering and drying in a current of carbonic anhydride: it burns into the sesquioxide when heated in the air.

(1021) **BISMUTHOUS OXIDE**, or *Sesquioxide of bismuth*; $Bi_2O_3 = 468$; *Density*, 8·211; *Comp. in 100 parts*, Bi, 89·74; O, 10·26.—This compound may be obtained in the anhydrous form, by heating the nitrate or the basic nitrate of the metal to low redness. It is a yellow, insoluble powder, which fuses at a red heat, and is easily reduced to the metallic state by heating it with charcoal. A white hydrate of this oxide, $Bi_2O_3.OH_2$, may also be prepared by precipitating a salt of bismuth by an excess of ammonia.

(1022) **BISMUTHIC OXIDE or ANHYDRIDE**, or *Peroxide of Bismuth*, $Bi_2O_5 = 500$, may be prepared by digesting the washed hydrated sesquioxide in a concentrated solution of potassic hydrate, and passing in chlorine gas. According to Arppe, a blood-red solution of potassic bismuthate is thus obtained, and a red precipitate is formed, which is to be well washed, and then digested in cold concentrated nitric acid to remove the bismuthous oxide with

which it is always mixed. A brilliant scarlet powder is thus left, which is bismuthic hydrate or bismuthic acid, $HBiO_3$; this loses water at 120° (248° F.), and is converted into the anhydride, Bi_2O_5, which is of a dull red colour. At a somewhat higher temperature it loses oxygen, and becomes converted into the intermediate oxide, or bismuthous bismuthate. According to Arppe, more than one of these intermediate oxides may be formed. Bismuthic acid is said to form salts with the alkali-metals, but these compounds are decomposed by merely washing them with water. Muir, however, who has recently examined the action of alkaline hydrates on bismuthic hydrate, was unable to obtain any salt of the bismuthic compound (Muir, *Jour. Chem. Soc.*, 1876, i. 151). The acid is decomposed by concentrated sulphuric acid at ordinary temperatures, and by nitric acid if the temperature be raised, oxygen being expelled and a salt corresponding to bismuthous oxide formed.

(1023) **BISMUTHOUS SULPHIDE**, or *Sesquisulphide of bismuth*, $Bi_2S_3=516$, occurs native as *bismuth glance* in delicate needles, and in crystals isomorphous with those of native antimonious sulphide. It may be formed artificially by fusing the metal with sulphur: a fusible dark grey compound, with a feebly metallic lustre, is thus obtained; in closed vessels it is decomposed into a subsulphide, and into free sulphur, which distils; in the open air sulphurous anhydride escapes, and bismuthous oxide remains. When solutions of bismuth are treated with sulphuretted hydrogen, a black precipitate of the sesquisulphide is formed. Bismuthous sulphide is dissolved by the metal in all proportions, a circumstance which affords an easy method of obtaining it in crystals, since the sesquisulphide crystallizes at a temperature at which the metal still remains fluid.

(1024) **BISMUTHOUS NITRATE**, or *Nitrate of bismuth*; $Bi3NO_3.5OH_2=396+90$; *Density*, 2·376.—This salt is the only other soluble compound of bismuth of any importance, and is easily prepared by dissolving the metal in nitric acid: it may be crystallized from the acid solution in large transparent prisms. If the solution, not too strongly acid, be largely diluted with water, an acid salt remains in the liquid, and a *subnitrate* falls, $Bi_2O_3.2HNO_3$, called by the old writers *magistery of bismuth*: another basic nitrate, $Bi_2O_3.HNO_3$, is also known. These basic nitrates appear to lose acid by washing.

(1025) **Characters of the Salts of Bismuth.**—Bismuth when in solution presents characters less marked than many metals. Its salts are colourless unless the acid be coloured; they are poisonous in large doses, and their solutions have an acid reaction; when diluted they become milky, owing to the formation of sparingly soluble basic salts, unless a large excess of acid be present. *Iron, zinc, copper,* and *tin,* throw down bismuth from its solutions in the metallic state. The *alkaline hydrates*

give a white precipitate of the hydrated sesquioxide, which is insoluble in excess of the precipitant, and becomes yellow by boiling it with the liquid. Solutions of the *carbonates, phosphates, tartrates,* and *ferrocyanides* give white precipitates with its salts. Bismuthous phosphate is insoluble in dilute nitric and acetic acids, and it has in consequence been proposed by Chancel as a convenient form in which phosphoric acid may be precipitated from acid solutions (516). This phosphate is, however, largely soluble in hydrochloric acid, whilst if sulphuric acid is present the precipitate generally becomes contaminated with basic bismuthous sulphate. *Sulphuretted hydrogen* throws down a black bismuthous sulphide, which is insoluble in ammonic hydric sulphide. *Potassic chromate* gives a yellow precipitate of *bismuthous chromate,* $Bi_2O_3.2CrO_3$, which is insoluble in potassic hydrate, but freely soluble in dilute nitric acid; it is thus distinguished from plumbic chromate. *Before the blowpipe* its salts are easily reduced on charcoal, and yield a brittle bead of bismuth, around which the yellow oxide is deposited.

(1026) **Estimation of Bismuth.**—Bismuth is estimated in the form of bismuthous oxide, Bi_2O_3, 100 parts of which correspond to 89·74 of the metal. Ammonic sesquicarbonate is its best precipitant, but the solution must not contain any chloride or hydrochloric acid, as an oxychloride of bismuth would in that case be precipitated, and a portion of the bismuth would be volatilized with the chlorine on ignition; the metal must in such a case be precipitated in the form of sesquisulphide. It may be separated from the alkalies, from titanium, and from all the metals of the first four groups (with the exception of cadmium), by means of sulphuretted hydrogen; the solution having been first acidulated with acetic acid. From tin, and from the metals of the fifth group, it may be separated by digesting the mixed sulphides (obtained by passing sulphuretted hydrogen through the liquid) in ammonic hydric sulphide, which leaves the bismuthous sulphide, and dissolves the other sulphides. The sesquisulphide must be dissolved in nitric acid, and precipitated by ammonic sesquicarbonate, which after standing for a few hours throws down the whole of the bismuth in the form of carbonate: it must be ignited in a porcelain crucible; carbonic anhydride is thus expelled, and bismuthous oxide, Bi_2O_3, remains.

Bismuth may be separated from cadmium by the addition of ammonia in excess to the solution of the sulphides in nitric acid; the cadmium is retained in solution, whilst the bismuth is precipitated.

CHAPTER XXIII.

GROUP VII.

COPPER, LEAD, THALLIUM, AND INDIUM.

Metals.	Symbol.	Atomic weight.	Atomic volume.	Specific heat.	Fusing-point. °C.	Fusing-point. °F.	Density.	Electric conductivity, 0° C.
Copper ...	Cu	63·4	7·08	0·0951	1091	1996	8·952	99·95
Lead ...	Pb	207·0	18·10	0·0314	325	617	11·38	8·32
Thallium ...	Tl	203·6	17·16	0·0335	294	561	11·862	9·16
Indium ...	In	113·4	15·28	0·0569	176	349	7·421	

THESE metals have no close chemical relationship. Thallium is a monad, and resembles silver in its specific heat, but is more like lead in physical properties and in some of its compounds.

§ I. COPPER: Cu″=63·4.

(1027) **COPPER** (Cuprum); *Density from* 8·921 *to* 8·952; *Fusing-pt.* 1091° (1996° F.); *Dyad in Cupric salts,* as $CuCl_2$; *Pseudo-monad in Cuprous salts,* as Cu_2Cl_2.—The ores of copper are numerous. The metal is frequently found native, crystallized in cubes, octahedra, or dendritic crystals; or else in masses, as in the North American and Siberian mines. In the neighbourhood of Lake Superior there is a vein of massive native copper, associated with silver (about 0·56 per cent.), but free from all other metals, so that it is especially valuable for wire for telegraphic purposes; this vein is in many parts two feet, or 0·6 metre, in thickness. The most common ore of copper, however, is the copper pyrites, or double sulphide of copper and iron, $Cu_2S.Fe_2S_3$, which occurs in the primitive rocks, and especially in the *killas,* or clay-slate. More rarely the pure cuprous sulphide, Cu_2S, is found in the mines of Cornwall and the Ural Mountains. Other less abundant ores are the blue and green carbonates, and the red and black oxides of copper.

The Cornish mines furnish more than half of the copper ore which is raised in Great Britain, but considerable supplies are received from Chili, Cuba, South Australia, and Spain. The most important seat of the copper smelting is Swansea, which sends forth annually from 18,000 to

20,000 tons of the refined metal. North America and Saxony supply the larger portion of the remainder. The Australian ore consists chiefly of the green and blue carbonate in a siliceous matrix; these ores contain from 25 to 35 per cent. of copper. Cuba furnishes both the oxides and the sulphides of the metal. Many of the ores from Chili are valuable on account of the large proportion of silver which they contain. The Cornish copper pyrites usually occur (mixed with small quantities of stannic oxide and arsenical pyrites) in a matrix of quartz, fluor-spar, and clay.

(1028) **Extraction of Copper from its Ores.**—The main object in the treatment of such an ore as the Cornish, is to oxidize and remove the sulphur and arsenic in the form of sulphurous and arsenious anhydrides, and to get rid of the quartz and oxide of iron in the form of a fusible slag, composed of silicate of iron combined with other earthy impurities, leaving metallic copper free from admixture.

After the ore has been raised from the mine it is sorted; the purest portions are broken into small pieces of the size of a hazel-nut, and the earthy portions are crushed and sifted, as in washing tin ore. The English ore is usually so mixed that it may contain an average of 8½ per cent. of copper.

The theory of copper smelting as practised at Swansea, like that of many other operations in the arts, is simple, although the working details have the appearance of being complicated.* The principal processes may, however, be enumerated as follows:

1. Calcining the ore.
2. Melting and granulating for coarse metal.
3. Calcination of the coarse metal.
4. Melting for fine metal.
5. Roasting of the fine metal for blistered copper.
6. Refining and toughening.

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* The apparent complication of the process arises from one of its great practical merits—viz., from the circumstance that it admits of being modified to suit almost every variety of ore, and these modifications necessarily tend to increase its complexity. Le Play enumerates six principal varieties of ores as being wrought by this method.—1. Pyritous ores, containing from 3 to 15 per cent. of copper. 2. Richer ores of the same kind, yielding from 15 to 25 per cent. of copper. 3. Siliceous oxides of copper, yielding from 12 to 20 per cent. of metal. 4. Oxides and carbonates with subsulphide of copper, in a siliceous matrix. 5. Very pure siliceous sulphides of copper and iron, yielding from 10 to 15 per cent. of copper; and 6. Pure sulphides and oxides of copper containing from 60 to 80 per cent. of the metal.

We shall make a few remarks upon each of these processes in succession.

(1029) 1. **Calcining the Ore.**—The calcination is conducted in large reverberatory furnaces, upon quantities of about 3 tons at a time; the heat is moderate, so as to avoid fusing the mass, which is spread evenly over the floor of the furnace, and stirred at intervals of 2 hours: this roasting is continued for 12 hours, at the end of which time the mass is converted into a black powder containing cuprous sulphide, oxide of iron, undecomposed sulphide of iron, and earthy impurities. Oxygen has a stronger attraction for iron than for copper, but the attraction of sulphur for copper is greater than for iron; and the effect of the roasting is seen in the production of ferric oxide and sulphurous anhydride, whilst the cuprous sulphide remains unacted upon. During this and the subsequent processes, large quantities of white fumes are given off, containing arsenious, sulphurous, and sulphuric anhydrides, hydrofluoric acid, and a certain portion of metallic arsenic. These deleterious fumes used to hang like a dense canopy over the smelting works and their vicinity; the cloud of *copper smoke*, as it is called, might be discerned at the distance of many miles: the ores are now, however, very frequently burnt in furnaces constructed so that the sulphurous anhydride is utilized for the manufacture of sulphuric acid instead of being allowed to escape to the injury of the surrounding neighbourhood. Where ores are of such a character that the proportion of sulphurous anhydride produced is too small to be available in the sulphuric acid manufacture, it is absorbed in coke towers moistened with soda solution, or in lime towers, as at St. Blasien in the Black Forest.

The *calcining furnace* employed in Wales is shown in section in fig. 360, and a plan of the hearth is exhibited in fig. 361. A is the fireplace; *b*, the bridge; *c c*, the hearth or roasting bed; *d, d*, are apertures in the floor, through which, by withdrawing an iron slide, the charge can be allowed to pass into the *cub*, or vault, E, when the roasting is complete; *f, f*, are the flues; *g* is an opening for the admission of air to the hearth; H, H, are the hoppers for charging the furnace, and *t*, a platform over which the barrows of ore are conveyed to the hoppers.

The fuel used in roasting the ore is chiefly anthracite, a coal which, under ordinary management, yields no flame. Flame, however, is absolutely necessary to the proper roasting of the copper ore: experience has taught the copper smelter to

obtain this desideratum by limiting the supply of air to the fuel in the fire-grate, thus causing the carbonic anhydride which is formed at the lower part of the fire to be converted into carbonic oxide. By a nice adjustment of the supply of

FIG. 360.

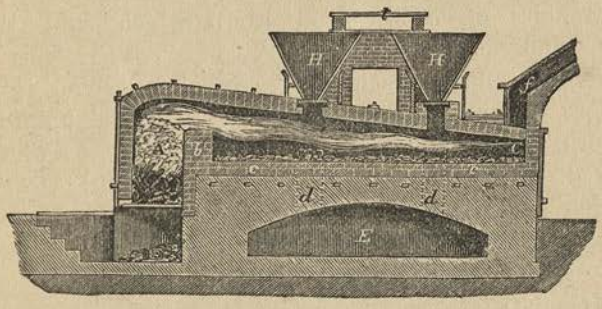
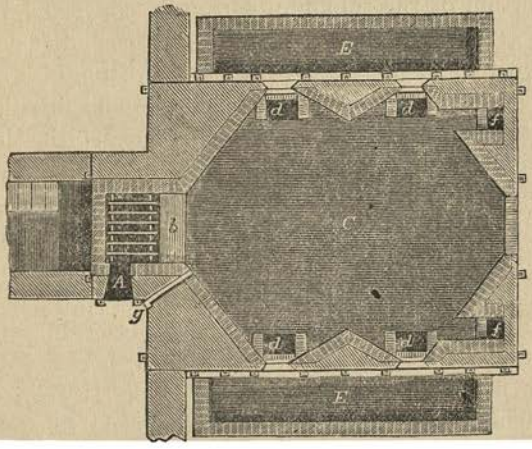


FIG. 361.



air through *g*, the other apertures of the furnace being closed, the carbonic oxide is gradually burned as it plays over the ore upon the hearth, *c c*; the maximum of heat is thus obtained at the minimum cost of fuel, the carbonic oxide being completely burned before it reaches the flue. An admirable analysis of this operation is given by Le Play in his elaborate memoir on the Welsh method of copper smelting (*Ann. des Mines*, [4], xiii. 128).*

* The heat emitted during the combustion of anthracite is very intense, so that it causes a rapid oxidation of the fire-bars of the furnace. This fuel has also the inconvenience of splitting into small fragments, which choke the air-

(1030) 2. **Melting for Coarse Metal.**—The roasted ore is now subjected to fusion in the *ore furnace* with certain proportions of slag, the produce of a subsequent operation, of siliceous ore free from sulphur, and of fluor-spar if necessary: by this means the charge is converted into a fusible slag, consisting chiefly of a ferrous silicate, and into sulphides of copper and iron, which sink through the slag, and form what is termed a *matt*. This fusion occupies about 5 hours, each charge containing about 1½ ton of roasted ore. The matt thus procured contains about 33 per cent. of copper: it is run off while liquid into water, by which it is granulated. The product goes by the name of *coarse metal*. The slag which floats above the matt is raked out of the furnace at a separate aperture. It ought to contain no appreciable quantity of copper.

(1031) 3. **Calcination of the Coarse Metal.**—The granulated metal is again roasted for 24 hours, during which operation a large proportion of the sulphide of iron is converted into oxide.

(1032) 4. **Melting for Fine Metal.**—A second fusion is performed upon this calcined matt with the addition of a portion of copper ore known to be rich in cupric oxide and in silica, and to contain but little iron pyrites. By this means the iron is removed in the slag in the form of silicate of iron, and the oxygen contained in the freshly added cupric oxide completes the oxidation of any portion of iron pyrites still remaining; the oxide of copper and the whole of the sulphide of this metal being brought to the state of cuprous sulphide, Cu_2S, or *fine metal*. The slags from this process and all the subsequent ones, are preserved. This matt, which contains about 80 per cent. of copper, is cast into pigs. If a very pure metal be required, the roasting is carried a little further; a portion of the metal is thus reduced: this portion con-

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ways between the bars, if the heat be suddenly applied. The copper smelter overcomes these difficulties by employing a grate consisting only of a few bars, which do not come into contact with the fuel itself, but only serve as a support for the clinker produced during the combustion of the coal. A bed of clinkers, 12 or 16 inches (30 or 40$^{cm.}$) thick, rests upon the fire-bars, and above this the fuel is burned: from time to time the fireman removes portions of the clinker as it accumulates.

Mr. Vivian has lately tried with success Gerstenhöfer's method of roasting these ores, in which they are supplied in a crushed state continuously to a furnace of special construction. The sulphur of the ore itself, after the furnace is lighted, maintains the necessary temperature for continuing the combustion, whilst the sulphurous acid is conducted into leaden chambers and converted into sulphuric acid.

tains the greater part of the foreign metals, which give up their sulphur more readily than the copper; the reduced metal, from its greater density, sinks to the bottom; the upper parts of the pigs are subsequently detached from the lower portions, and the metal extracted from the upper portions of the ingots is known in the market as *best selected copper*.

(1033) 5. **Roasting for Blistered Copper.**—The fine metal or cuprous sulphide is now to be freed from the sulphur, which has hitherto been useful by forming a fusible compound with the copper, thus facilitating its separation from the impurities by which it was accompanied. With this view the pigs of fine metal are next subjected, for several hours, upon the bed of a reverberatory, to a heat just short of that required to fuse them; the metal by this means becomes oxidized at the surface, and a part of the sulphur which it still retains is also oxidized; at last it is fused: a remarkable reaction then begins to take place. When cupric oxide and cuprous sulphide are heated together, they decompose each other, sulphurous anhydride and metallic copper being produced, $Cu_2S + 2CuO = SO_2 + 4Cu$. It is not desirable that the temperature should be too strongly raised, as the cupric oxide would then combine with the silica still present in the mass, and would cease to exert its oxidizing influence. After the charge has become liquid, the temperature of the furnace is allowed to fall; the melted mass solidifies upon its surface, and an appearance of violent ebullition is produced from the formation of sulphurous anhydride and its efforts to escape from the tenacious mixture: when this ceases, the desulphuration is complete. The heat is now rendered very intense, the copper melts and sinks to the bottom, and separates completely from the slag, which consists chiefly of cuprous silicate; the reduced metal is then run off into sand moulds. The ingots thus obtained, being full of bubbles, are termed *pimple* or *blistered copper*.

(1034) 6. **Refining or Toughening.**—The blistered copper now undergoes the concluding operation of refining. From 7 to 8 tons, or about 8000 kilos., of the metal are placed in a reverberatory furnace and kept in a melted state for upwards of 20 hours, in order to oxidize the last traces of foreign metals: during this process a large quantity of cuprous oxide is formed; part of this oxide is absorbed by the melted metal, and the copper, if examined at this stage, is found to be of a dull red colour, coarse grained and brittle. To reduce this oxide, the slags are skimmed off, and the surface is covered with a few shovelfuls of anthracite or charcoal; the metal is then subjected to the process of *poling*, in

which the trunk of a young tree is thrust into the molten metal. The inflammable gases disengaged from the green wood as it chars, produce a powerful agitation of the whole mass, and in about 20 minutes the poling is finished; the reducing influence of the combustible gases having in the meantime been brought to bear upon every portion of the melted metal. In this way the oxide diffused through the mass is deprived of oxygen. If the poling be carried too far, the copper again becomes brittle, and is said to be *overpoled*. This defect may be remedied by exposing the surface of the melted metal to a current of air. If too little poling be used, the metal is still brittle, and it is then said to be *underpoled*. The progress of the poling, therefore, requires careful watching: the refiner tests the metal from time to time by dipping a small test-ladle into the melted mass, and the sample of copper thus removed is cooled suddenly by immersion in water: the grain of the copper is judged of by cutting the hammered button partially through with a chisel or shears, and then bending it by placing it in a vice. If properly refined, the broken surface will display a fibrous structure with a beautiful silky lustre. If underpoled, the fracture will be granular, with a number of red points. If overpoled, the fibres become coarser, and the fracture has a strong metallic lustre, but the silky appearance is wanting. When, upon testing, the copper appears to be fine grained, fibrous, and silky, of good colour, and malleable, it is either ladled out and cast into ingots; or it is cooled suddenly at the surface, by allowing water to run upon it; in the latter case *rose copper* is produced, and successive films are made and removed until all the metal is consumed. There appears to be no doubt that the brittleness of underpoled copper is due to the presence of red oxide of copper in the metal, and Mr. Vivian has suggested that overpoled copper may be defective from the presence of a little carbon. Percy, however, was unsuccessful in the attempt to discover carbon in overpoled specimens. An interesting paper by Abel on the non-metallic impurities of refined copper will be found in the *Jour. Chem. Soc.*, 1864, xvii. 164.

The slags from the various operations are carefully remelted, and the copper which is extracted from them is termed *black copper;* it is run into pigs, which are subsequently refined.

The presence of a small quantity of tin in the refined copper is considered to be advantageous, as the toughness and tenacity of the metal are thereby increased. Antimony is singularly injurious; so small a quantity as 1 part in 3600, or 10 ounces in the ton, renders copper unfit for making brass that is required for

rolling; and minute traces of nickel and of bismuth are also said greatly to injure the tenacity of the metal.

In Sweden and in the Mansfeld district of Prussian Saxony a species of blast furnace is employed in some of the operations of copper smelting.

The copper of commerce is often very nearly pure. It contains minute quantities of arsenicum, of iron, of lead, and sometimes of tin and silver. Abel has detected traces of selenium in some specimens, and of sulphur in others. Copper may be readily obtained in a state of perfect purity, by decomposing a solution of pure cupric sulphate by means of the voltaic battery: it is then deposited upon the negative electrode in coherent plates.

(1035) **Kernel Roasting.**—When cupriferous iron pyrites containing from 2 to 3 per cent. of copper, is broken into lumps of about the size of the fist, and subjected to a very gradual roasting, a large portion of the copper becomes concentrated in the middle of the lump, and a nucleus of sulphide of copper and iron is formed. This nucleus, or *kernel*, is surrounded by a more or less porous shell, composed mainly of ferric oxide, which may be detached from the nucleus by a blow. Upon these observations a method of roasting copper ore has been founded, to which the name of *kernel roasting* has been given. This roasting is conducted in the Venetian Alps, at Agordo, in kilns, and at Mülbach in enormous heaps in the open air. These heaps are in the form of a truncated square pyramid, the base of which is 9 or 10 metres, or about 30 feet square (p. 189). The roasting is a very slow operation, requiring from 5 to 6 months for its completion. Spring and autumn are the most favourable seasons in which to commence it. Sulphur distils off to the extent of about 1 per cent. of the ore; the kernels constitute from 13 to 14 per cent. of the roasted mass, and they contain about 5 per cent. of metallic copper. The cause of this concentration of copper in the interior of the mass is entirely unexplained. The shells, which retain a small proportion of cupric sulphate, are washed to extract this as far as practicable, and the roasted ore is then subjected to processes not essentially differing from those already described (Percy, *Metallurgy*, i. 439).

In many copper mines the water which is pumped up is impregnated with cupric sulphate derived from the oxidation of the sulphide by exposure to the air: the copper is easily separated in the metallic form, by collecting the water in tanks containing scrap iron, the iron displacing the copper from the salt: $CuSO_4 + Fe = FeSO_4 + Cu$.

When the ore consists of the oxides and carbonates of copper, it is easily reduced to the metallic state by simple fusion with coke or charcoal, ferric oxide and lime being added in quantity sufficient to form a fusible slag with the silica which usually accompanies these ores; the copper is rendered tough by a process analogous to that of poling.

(1036) **The Wet Process.**—Mr. Henderson has recently introduced a process by which a good deal of copper is now extracted from a pyrites poor in copper. This pyrites, after it has been burned for the sake of its sulphur in the manufacture of oil of vitriol, furnishes a mass consisting chiefly of oxide of iron mixed with about 3 per cent. of copper, and from 6 to 8 per cent. of sulphur, with small quantities of arsenic, and sometimes of zinc and bismuth; the proportion of sulphur must be about 3 parts for every 2 parts of metal to be

removed. It is ground to a fine powder after admixture with about 15 per cent. of salt, or about twice as much salt as of metal to be extracted. The mixture is then roasted for some hours at a low red heat. Copious fumes of hydrochloric acid, and free chlorine, mixed with chlorides of iron, arsenic, and other volatile metals are evolved, whilst the greater part of the copper is converted into chloride, and the sodic chloride into sodic sulphate:

$2NaCl+Cu_2S+2O_2=Cu_2Cl_2+Na_2SO_4$; or $2NaCl+CuS+2O_2=CuCl_2+Na_2SO_4$: $6NaCl+Fe_2S_3+6O_2=Fe_2Cl_6+3Na_2SO_4$; and $2Fe_2Cl_6+3O_2=2Fe_2O_3+6Cl_2$.

The roasted mass is lixiviated first with water, and then with weak acid, and finally is washed with water. The oxide of iron which is left is used for lining puddling furnaces (p. 622). The liquors which contain the copper in solution are treated with scrap iron, and the copper which is precipitated is collected and refined by poling in the usual way.

(1037) **Properties of Copper.**—Copper is one of the metals which has been longest known to man: before the art of working iron was understood, it was in extensive use, either alone or alloyed with tin, for many of the purposes to which iron is now applied. It is of a well known red colour, and has a peculiar, disagreeable odour and taste when moistened and rubbed. It is rather a hard metal, very tenacious, ductile, and malleable; after it had been melted beneath a layer of common salt, to exclude atmospheric air, pure copper was found by Scheerer and Marchand to have a density of 8·921: this was increased by hammering, and when drawn into fine wire it was obtained as high as 8·952: Daniell estimated its fusing-point at 1091° (1996° F.). When heated to a temperature approaching its melting point it becomes so brittle that it may be reduced to powder, and an ingot may be broken by a blow from a hammer. If exposed to a very intense heat, copper is capable of volatilization, but it is usually considered to be fixed in the fire (550). By slow voltaic action it may be obtained crystallized in cubes and octahedra, and is sometimes found native in these forms. It ranks amongst the best conductors of heat and electricity. If heated to redness in the open air, copper combines with oxygen rapidly, a layer of oxide is formed upon the surface, and as the oxide contracts more slowly than the metal beneath, it scales off if suddenly cooled, leaving a bright, clean, metallic surface. Copper is not oxidized when heated to redness in a current of steam. Exposure to a moist air at ordinary temperatures has no effect upon copper; neither has pure water; but in sea water, or in solutions of the chlorides, it is gradually corroded, with the formation of cupric oxychloride: even ordinary spring and river waters attack copper in many instances, so that it is unsafe to employ copper pipes to convey water used for culinary purposes. Finely-divided copper,

when touched with a glowing coal, becomes ignited and burns like tinder, being converted into the black oxide. Chlorine readily combines with the metal, thin leaves of which take fire spontaneously in the gas. Nitric acid oxidizes and dissolves copper with rapidity. Oil of vitriol does not act upon it in the cold, but if heated with it, the acid is decomposed, sulphurous anhydride being evolved and cupric sulphate formed. Hydrochloric acid dissolves it if air have access to the mixture, but if air be excluded, it has no such effect at ordinary temperatures; when boiled, however, with the finely-divided metal, it dissolves it very slowly, hydrogen being evolved (Odling). Copper also decomposes hydrochloric acid when heated to redness in a current of the gas, cuprous chloride being formed and hydrogen liberated. The fixed alkalies have little action on copper, but ammonia gradually dissolves the metal if air has access to it, slow oxidation taking place. Before the oxyhydrogen blowpipe it burns with a green flame, and if introduced into the flame of gas or of alcohol it communicates to it a green colour.

Uses.—The applications of copper in the arts are very numerous. Independently of its use in coinage, vast quantities of it are annually consumed in the sheathing of ships* and in the manufacture of boilers, and of various utensils for domestic purposes. It also forms the basis of a number of valuable alloys in extensive use: with zinc it furnishes the different varieties of brass; and with different proportions of tin, it forms bronze, bell-metal, gun-metal, and speculum metal (924); whilst its oxides and salts are largely employed as pigments, and yield articles of some importance in the materia medica.

Silicide of Copper.—A compound of copper and silicon containing 12 per cent. of the latter may be obtained by fusing together 3 parts of potassic silicofluoride, 1 part of sodium, and 1 of copper turnings: it is hard, brittle, and white, like bismuth. Another alloy may be obtained by prolonged heating of a mixture of sand, charcoal, and copper; when it contains 4·8 per cent. of silicon it is of a fine bronze colour. It is as fusible as bronze, very ductile, and yields a wire a little softer than iron, but quite as tenacious; it may be worked well at the lathe.

(1038) **Alloys of Copper.**—The combination of zinc with copper has a yellow colour, the tint of which becomes paler in proportion as the quantity of zinc is increased. A curious observation upon this point was made by D. Forbes, who found

* Percy's experiments appear to show that the presence of a small quantity of phosphorus in the copper has some effect in protecting the metal from the corrosive action of sea water.

that a brittle, crystalline alloy of a silver-white colour may be formed, containing 53·49 per cent. of zinc, and consisting of 7 atoms of copper, to 8 of zinc; but if the quantity of zinc were either increased or diminished, the alloy had the usual yellow colour of brass. The density of brass is greater than the mean of that of the metals which form it. Ordinary brass has a density of 8·29; it contains about 64 per cent. of copper, being nearly Cu_2Zn. Brass which contains 25 per cent. of zinc melts at 954°·4 (1750° F.; Daniell), and a larger proportion of zinc increases its fusibility. By long continued exposure to a high temperature in closed vessels, the whole of the zinc may be expelled, and it is not possible to fuse the alloy without losing a portion of the zinc. The alloys of zinc and copper are malleable when cold, but are generally brittle when hot. An alloy largely used under the name of *Muntz metal*, or *yellow metal*, for the sheathing of ships, may be rolled whilst hot: it contains 2 atoms of zinc to 3 of copper, or 60 per cent. of copper. The addition of about 2 per cent. of lead to brass improves its quality if it is to be worked at the lathe; it diminishes its toughness, and prevents it from hanging to the tool and clogging the file: but if intended for wire, the presence of lead must be avoided. A very small proportion of tin, even if it does not amount to 1 part in 200, greatly increases the hardness of the alloy. The ordinary *hard solder* for brass is an alloy consisting of 2 parts of brass and 1 of zinc. Brass is usually made by melting granulated copper in crucibles with rather more than half its weight of zinc; formerly a mixture of calamine and charcoal was substituted wholly or partially for metallic zinc. At Swansea, the Muntz metal is prepared by melting the two metals in a reverberatory furnace, which enables a large quantity of the alloy to be prepared with rapidity; but the process is attended with a considerable waste of zinc. Bronze and the other alloys of copper with tin have already been described (p. 695).

Gedge's and Aich's alloys consist of a mixture of copper, zinc, and iron, which can be forged, cast, rolled, or drawn into wire; 100 parts of the best description of Gedge's alloy contain—copper 60 parts, zinc 38·2, and iron 1·8 parts. It is very hard, and appears to be well adapted to the sheathing of ships. It acquires great stiffness and elasticity if worked cold, but may be softened by annealing. Another alloy of a similar kind, termed *sterro metal*, consists of copper 55·04, zinc 42·36, iron 1·77, and tin 0·83 parts.

(1039) **CUPROUS HYDRIDE,** Cu_2H_2.—This substance was obtained by Wurtz, as a brown hydrate, when hypophosphorous acid was mixed with a solution of cupric sulphate, and heated to about 60° (140° F.), or by adding a

hypophosphite to an acidulated solution of cupric sulphate. It is very unstable: when dry it is suddenly resolved at 70° (158° F.), into hydrogen gas and finely-divided metallic copper. It takes fire spontaneously in gaseous chlorine. Hydrochloric acid forms with it cuprous chloride, attended with a brisk disengagement of hydrogen. This disengagement of hydrogen gas from the acid as well as from the hydride is remarkable; Brodie explains it by supposing that the hydrogen of the hydride and that in the acid are in opposite electrical or polar conditions, in consequence of which they unite at the moment of liberation and form *hydride of hydrogen*, or hydrogen gas; thus, $Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2HH$.

(1040) **CUPROUS CHLORIDE**, or *Subchloride of copper*, $Cu_2Cl_2 = 197{\cdot}8$; *Density*, 3·376.—Copper forms two compounds with chlorine, Cu_2Cl_2, and $CuCl_2$, the former of which, cuprous chloride, may be obtained by distilling copper filings with twice their weight of corrosive sublimate; or by dissolving 4 parts of finely-divided copper and 5 of the black oxide in hydrochloric acid; or by boiling cupric chloride with stannous chloride or with sugar; or by digesting cupric chloride in closed vessels with metallic copper: the last is a slow process, but part of the cuprous chloride is then deposited in transparent tetrahedra: on passing sulphurous anhydride into a solution of equivalent quantities of cupric sulphate and sodic chloride, cuprous chloride is precipitated as a crystalline powder consisting of tetrahedra. These are exceedingly sensitive to light, an exposure of a few minutes to direct sunshine being sufficient to cause them to assume a copper colour and metallic lustre. Cuprous chloride may also be obtained by boiling a solution of cupric chloride, or a mixture of cupric sulphate and sodic chloride, with metallic copper, and then pouring it into water, when the cuprous chloride is thrown down as a white crystalline precipitate; or by heating dry cupric chloride in a current of dry ammonia until the whole is converted into a yellowish liquid; this solidifies on cooling to a white mass, consisting of the pure chloride (Millon and Commaille, *Ann. Chim. Phys.*, 1864, [4], iii. 285). Cuprous chloride is a white compound, which fuses easily into a yellowish mass, and darkens by exposure to light when moist. It is insoluble in water, but soluble to some extent in strong hydrochloric acid, forming a colourless solution, which deposits most of the subchloride on dilution. The solution of cuprous chloride in hydrochloric acid absorbs carbonic oxide gas with facility: a compound crystallizing in pearly scales ($4Cu_2Cl_2{\cdot}3CO{\cdot}7OH_2$?; Berthelot) may thus be obtained; water decomposes it, setting cuprous chloride at liberty: it is also quickly altered by exposure to the air. Cuprous chloride is soluble in a boiling solution of potassic chloride; and if the liquid be allowed to cool without

access of air, octahedral crystals, composed of $4KCl.Cu_2Cl_2$, are deposited. When the solution in hydrochloric acid is exposed to the air, it absorbs oxygen rapidly, becoming brown, and a pale bluish-green insoluble cupric oxychloride, $CuCl_2.3CuO.4OH_2$, is deposited. This oxychloride is used in the arts as a pigment, under the name of *Brunswick green*. It is most conveniently prepared by exposing copper clippings to the action of hydrochloric acid, or to a solution of sal ammoniac in the open air. It occurs native in the form of a green sand (*density* 4·4), composed of small rhombic prisms, which is found at Wallaroo in Australia, and at Atacama in Peru; it has hence been called *atacamite*. Sometimes it is found massive. Other oxychlorides of copper of less importance may also be formed.

When finely-divided copper is boiled with a solution of ammonic chloride, ammonia is expelled, and a salt is formed which is gradually deposited in white rhombic dodecahedra, $N_2H_6.Cu_2Cl_2$: it may be regarded as the dichloride of cuproso-diammonium, $N_2H_6(Cu_2)''Cl_2$. A solution of this salt, when exposed to the air, deposits blue crystals consisting apparently of a double chloride of cuproso-diammonium and cupro-diammonium, $N_2H_6(Cu_2)''Cl_2.N_2H_6Cu''Cl_2$; and the mother-liquor on further exposure yields cubic crystals of the double chloride of cuprammonium and ammonium, $N_2H_6Cu''Cl_2.2NH_4Cl$.

(1041) **CUPRIC CHLORIDE**, or *Chloride of copper*, $CuCl_2$= 134·4 (*density*, 3·054), may be obtained by the spontaneous combustion of copper in chlorine, but it is more conveniently prepared by dissolving cupric oxide or carbonate in hydrochloric acid, and evaporating the solution; it then crystallizes in needles, with the formula $CuCl_2.2OH_2$, of density 2·534: these appear of a grass-green colour as long as a trace of moisture adheres to them, but when dried in a vacuum over sulphuric acid are transparent, and of a beautiful pale blue colour. A concentrated solution of cupric chloride is of a green colour, but it becomes blue on dilution, and when the salt is anhydrous it is liver-coloured. When heated it fuses, and at a red heat half its chlorine is expelled, cuprous chloride remaining. It forms double chlorides with the potassic and ammonic chlorides. Cupric chloride is deliquescent, and very soluble in alcohol: this solution burns with a splendid green flame, the spectrum of which is shown in Fig. 81, No. 5; Part I. p. 187.

A *double chloride of copper and ammonium*, $2NH_4Cl.CuCl_2.2OH_2$, is obtained in blue square-based octahedra, by mixing hot concentrated solutions of the two salts in the proportion of 2 molecules of ammonic chloride and 1 of cupric chloride. Another double chloride, $NH_4Cl.CuCl_2.2OH_2$, is obtained in fine, bluish-green crystals, by evaporating a solution of equal molecular weights of the two salts.

Anhydrous cupric chloride absorbs ammonia rapidly, and forms a blue powder ($CuCl_2.6NH_3$; Rose), which by a heat of 150° (302° F.), loses 4 molecules of ammonia, and becomes green ($CuCl_2.2NH_3$; Kane). Graham and Kane regard this latter compound as ammonic chloride in which the fourth atom of hydrogen has been replaced by copper; hence Graham terms it *chloride of cuprammonium*, $(N_2H_6Cu'')''Cl_2$. If gaseous ammonia be passed through a hot concentrated solution of cupric chloride, until the precipitate at first formed is redissolved, the liquid on cooling deposits small dark-blue, square prisms and octahedra, $N_2H_6Cu''Cl_2.(NH_4)_2O$.

It appears that the following well-defined compounds may be obtained by the reaction of the chlorides of copper upon ammonia or ammonic chloride:

(1.) $[N_2H_6(Cu_2)'']''Cl_2$
(2.) $[N_2H_6(Cu_2)'']''Cl_2.(N_2H_6Cu'')''Cl_2.OH_2$
(3.) $(N_2H_6Cu'')''Cl_2$, or $CuCl_2.2NH_3$
(4.) $(N_2H_6Cu'')''Cl_2.NH_3$, or $CuCl_2.3NH_3$
(5.) $(N_2H_6Cu'')''Cl_2.2NH_3$, or $CuCl_2.4NH_3$
(6.) $(N_2H_6Cu'')''Cl_2.3NH_3$, or $CuCl_2.5NH_3$
(7.) $(N_2H_6Cu'')''Cl_2.4NH_3$, or $CuCl_2.6NH_3$
(8.) $(N_2H_6Cu'')Cl_2.(NH_4)_2O$
(9.) $(N_2H_6Cu'')Cl_2.2NH_4Cl$
(10.) $2NH_4Cl.Cu''Cl_2.2OH_2$
(11.) $NH_4Cl.Cu''Cl_2.2OH_2$.

Various other salts of these cuprammoniums besides the chlorides have been obtained.

(1042) **BROMIDES OF COPPER.**—*Cuprous bromide*, or *Subbromide of copper*, Cu_2Br_2, is insoluble in water. *Cupric bromide*, $CuBr_2$, is soluble.

(1043) **IODIDES OF COPPER.**—*Cuprous iodide*, or *Subiodide* of copper, $Cu_2I_2.OH_2$, is a white insoluble powder, which becomes yellow when heated. It is formed by pouring a mixture of 1 equivalent of ferrous sulphate, and 1 of cupric sulphate into a solution of any iodide; thus $2CuSO_4 + 2FeSO_4 + 2KI = Cu_2I_2 + K_2SO_4 + Fe_23SO_4$. Sodic sulphite may be substituted for the ferrous sulphate in this experiment. It has been proposed to employ such a mixture of the ferrous and cupric sulphates as a test for determining the quantity of iodine in kelp, in order to fix its commercial value. Cuprous iodide is also slowly produced by the long-continued action of hydriodic acid on metallic copper. *Cupric iodide*, CuI_2, if it exists, is very unstable.

(1044) **OXIDES OF COPPER.**—There are two salifiable oxides of copper, both of which are found in the native state; viz., the red or *cuprous oxide*, Cu_2O, and the black or *cupric oxide*, CuO; this last is the basis of the ordinary salts of the metal. Rose discovered the existence of a still lower oxide, which he terms a *quadrantoxide*, $Cu_4O.xOH_2$; it is only known as an olive-green hydrate of extreme oxidability, obtained by digesting a cupric salt in closed vessels for 24 hours with an excess of stannous chloride dissolved in a large excess of potassic hydrate. Some indications have been obtained of the existence of a still higher oxide than CuO, probably Cu_2O_3.

(1045) **CUPROUS OXIDE,** *Red oxide* or *Suboxide of copper;* $Cu_2O = 142{\cdot}8$; *Density,* 5·75; *Comp. in* 100 *parts,* Cu, 88·8; O, 11·2.—This compound occurs native, crystallized either in the octahedron, or in some of its derived forms, or else in capillary crystals or lamellar masses. There are various ways of obtaining this oxide artificially; one of the best consists in boiling the dibasic cupric acetate with sugar; the cupric oxide is thus deprived of half its oxygen, and the red oxide is deposited in small octahedra. Another method consists in digesting copper foil in a solution of a salt of copper such as the sulphate, mixed with a large excess of ammonia, and warming the mixture in a vessel completely excluding the air, the liquid becomes decolorized, and deposits the suboxide as a reddish-yellow powder. It may also be obtained by igniting 5 parts of powdered cupric oxide with 4 parts of copper filings, in a covered crucible. The red oxide fuses at a full red heat. By decomposing cuprous chloride with potassic hydrate it is obtained as an orange-yellow hydrate ($4Cu_2O.OH_2$; Mitscherlich). In this condition it is readily attacked by acids.

A cuprous sulphate, carbonate, and acetate appear also to exist. The cuprous salts are unstable, and absorb oxygen readily. Some of its double salts are more stable; a *cuprous potassic sulphite,* $Cu_2SO_3.2K_2SO_3$, may be obtained as a yellow insoluble precipitate, by mixing solutions of normal or of hydric potassic sulphite with cupric sulphate; in this case, the cupric salt is reduced to the state of a cuprous salt by the sulphite.

Cuprous oxide is soluble to some extent in metallic copper, which it renders, in technical terms, *dry,* or brittle. Abel found as much as 4·6 per cent. of cuprous oxide in a specimen of very *dry* copper which he examined.*

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* Abel has contrived a method of determining the amount of oxide in the metal, founded upon the fact that cuprous oxide decomposes neutral argentic nitrate, furnishing an insoluble basic cupric nitrate, $Cu_2O + 2AgNO_3 = Ag_2 + Cu2NO_3.CuO$: this basic salt is soluble in dilute sulphuric acid: $Cu2NO_3.CuO + 2H_2SO_4 = 2CuSO_4 + 2HNO_3 + OH_2$. The plan consists in digesting 500 or 600 grains (30 or 40 grams) of the copper for trial in a solution of 400 grains (25 grams) of neutral argentic nitrate in the cold, for three or four hours. The undissolved portion of copper is removed, washed into the solution of silver, dried, and weighed. The mixture of precipitated silver and insoluble basic cupric nitrate is separated by decantation from the solution, then washed, and digested with frequent agitation for half-an-hour with a known quantity of standard sulphuric acid. It is filtered, and the washings neutralized by sodic carbonate. The proportion of acid neutralized by the basic cupric nitrate furnishes the means of estimating the quantity of cuprous oxide, 80 parts of SO_3 being equivalent to 16 parts of oxygen in the sample, or to 142·8 of cuprous oxide.

The anhydrous suboxide is resolved by most of the stronger acids into a cupric salt, and metallic copper. Nitric acid converts it into cupric nitrate: but hydrochloric acid changes it into cuprous chloride, which is soluble in excess of the acid. Hydrated cuprous oxide is soluble in a solution of ammonia, forming with it a colourless liquid. This solution is an extremely delicate test of the presence of oxygen in a gaseous mixture; a mere trace of oxygen causes it to assume a blue tint from the formation of cupric oxide, which when dissolved in the solution of ammonia has an intense blue colour. An ammoniacal solution of cuprous chloride, when mixed with a solution of argentic nitrate containing a large excess of ammonia, immediately deposits reduced silver in a fine state of subdivision, whilst argentic chloride and cupric nitrate are held in solution in excess of ammonia; $Cu_2Cl_2 + 4AgNO_3 = 2(Cu2NO_3) + 2AgCl + Ag_2$. The principal employment of cuprous oxide is in the manufacture of stained glass, to which it imparts a beautiful ruby or purple colour.

(1046) **CUPRIC OXIDE**, or *Black oxide of copper*, CuO = 79·4; *Density*, 6·5; *Comp. in* 100 *parts*, Cu, 79·85; O, 20·15.—This oxide is a compound of considerable importance to the chemist. It is employed largely as a means of furnishing oxygen for the combustion of carbon compounds in organic analysis. The best process for obtaining cupric oxide is to dissolve copper in pure nitric acid, and decompose the resulting nitrate by heating it to redness in an earthen crucible; the water and nitric acid are thus expelled, and the black oxide remains in a state of purity: the heat should be long continued, but not too violent; otherwise the oxide sinters together and concretes into hard masses, which are pulverized with difficulty. A very pure oxide is also furnished by the decomposition of the carbonate by heat; or still more simply by strongly igniting copper in a muffle for some hours, or by heating a plate of copper to redness in a brisk current of air, and suddenly quenching it in water, in which case the oxide separates in black scales, the inner layer of which often contains a little red oxide. It may be obtained as a hydrate of a light blue colour, CuH_2O_2, from any of its salts, by the addition of a slight excess of potassic hydrate, washing quickly with cold water, and drying at ordinary temperatures: when boiled with water the oxide becomes black and anhydrous. This hydrate is soluble in an excess of a solution of ammonia, forming a liquid of a splendid blue colour: if slips of metallic copper be introduced into a bottle which is filled with this solution, and closed so as completely to exclude the air, a portion of the metal

equal to that already in solution is dissolved, the metal deriving oxygen from the oxide already in solution, both portions being thus reduced to the state of cuprous oxide; $Cu + CuO = Cu_2O$; the colour gradually disappears, since cuprous oxide produces a colourless solution with ammonia; but the moment that air is admitted, the blue colour is reproduced. Cupric oxide is soluble in oils and fats, so that greasy matters boiled in a copper saucepan which is not kept bright are liable to become impregnated with the metal. Cupric oxide combines with glass, and imparts to it a beautiful green colour. The oxide is hygroscopic, particularly if in a finely-divided state, and it absorbs water rapidly from the air. Its oxygen cannot be expelled from it by mere exposure to heat, but if the oxide be plunged into an atmosphere of hydrogen while warm, it is decomposed with evolution of light and heat, water being formed. Cupric oxide is soluble in most of the acids, and combines with them to form salts which have a green or a blue colour. When fused with potassic or sodic hydrate, cupric oxide combines with the alkali, forming a greenish-blue mass, which is decomposed by the addition of water.

Thénard obtained a combination of peroxide of hydrogen with cupric oxide; it was of a yellowish-brown colour, and when moist quickly underwent decomposition at ordinary temperatures.

(1047) **TRICUPRIC NITRIDE**, Cu_6N_2, is obtained by passing a current of dry gaseous ammonia over finely-powdered cupric oxide heated at 250° (482° F.); water and nitrogen gas are evolved, and the nitride is left as a dark green powder, which when heated to about 310° (590° F.) explodes feebly, emitting a red light; strong acids decompose it with evolution of nitrogen.

(1048) **SULPHIDES OF COPPER.**—These are three in number: Cu_2S; CuS; and CuS_5.

Cuprous Sulphide, or *Subsulphide of copper*, $Cu_2S = 158{\cdot}8$ (*density* 5·5—5·977), is a soft mineral of a dark grey colour, occasionally found native in masses as *copper glance*, but more frequently in six-sided prisms. It is easily fused by heat in closed vessels; nitric acid and aqua regia decompose it readily, but hydrochloric acid does not dissolve it. It may be formed by melting together 3 parts of sulphur and 8 of copper; vivid incandescence occurs at the moment of combination. It forms the *fine metal* of the copper smelter.

Cupric Sulphide, or *Sulphide of copper*, $CuS = 95{\cdot}4$, may be prepared by the direct union of its constituents, or by exposing copper turnings to the action of a solution of sulphur in carbonic bisulphide; it is also occasionally found native, as *indigo copper*, in flexible plates of a blue colour (*density*, 3·85). It may likewise be obtained in the form of a dark-brown hydrate, by decom-

posing a salt of copper by a stream of sulphuretted hydrogen: this hydrate is quickly oxidized by exposure to the air, being converted into cupric sulphate; it is easily dissolved by nitric acid and by aqua regia. Cupric sulphide is insoluble in a solution of dipotassic sulphide, but it is slightly soluble in diammonic disulphide, $(NH_4)_2S_2$.

Copper Pyrites (*density*, 4·1—4·3) or ordinary ore of copper, consists of a double sulphide of copper and iron, $CuFeS_2$. It is of a yellow colour, and has a brassy lustre: it is sometimes found crystallized in tetrahedra, but it usually occurs in amorphous masses, with a conchoidal granular fracture, and is less hard than iron pyrites. The variety called variegated or *peacock ore* contains a larger proportion of sulphide of copper. These compounds are rapidly oxidized and dissolved by nitric acid or by aqua regia, but not by hydrochloric acid.

All the sulphides of copper are decomposed by roasting them in the air; if the temperature be high, sulphurous anhydride escapes, and cupric oxide remains behind; at a lower temperature, cupric sulphate is formed.

Cupric sulphide likewise forms a natural combination with sulphides of lead, silver, antimony, and arsenicum, constituting grey copper ore, or *fahlerz*: this mineral is essentially a tetrabasic sulphantimonite and sulpharsenite of copper and iron; it varies considerably in the relative proportions of its constituents, and often contains zinc, lead, silver, and mercury. It crystallizes in forms derived from the regular tetrahedron, and in composition it corresponds to the general formula $(MS)_4.R_2S_3.(M_2S)_4.R_2S_3$, in which M represents the electropositive metals, M_2S being usually cuprous or argentic sulphide: whilst R indicates the electronegative metals arsenic or antimony. The principal varieties of the ore are:—1. *Tennantite*, $FeS.(CuS)_3.As_2S_3.(Cu_2S)_4.As_2S_3$ (*density* 4·375), a ferrous and cuprous sulpharsenite, of a leaden-grey colour; the copper in this ore amounts to about 48 per cent. 2. *Light-grey copper ore* (*density* 4·5 to 4·7), a mixture of sulpharsenite and sulphantimonite of zinc, iron, copper, and silver: colour, steel-grey. 3. *Dark-grey copper ore* (*density* 4·7 to 4·9) contains little or no arsenic; it is of an iron-black colour. This variety and the one preceding it contain from 35 to 40 per cent. of copper. 4. *Silver fahlerz* (*density* about 5·0), is a dark-grey copper ore, rich in silver. The silver varies in this ore from 13 to 30 per cent., and the copper from 14 to 25 per cent.

Cupric Pentasulphide, CuS_5, was obtained by Berzelius in the form of a blackish-brown precipitate, by decomposing a cupric salt with a pentasulphide of one of the alkali-metals. It undergoes no change by washing when exposed to the air, but is completely soluble in a solution of potassic carbonate.

SELENIDE OF COPPER.—A native selenide of copper is found in combination with selenide of silver. It occurs in masses of a leaden-grey colour, and is very rare, having hitherto been found only in Sweden: selenide of copper may be formed artificially by precipitating the cupric sulphate by seleniuretted hydrogen.

(1049) **PHOSPHIDE OF COPPER,** Cu_2P_2.—This compound is easily obtained by boiling phosphorus in a solution of cupric sulphate; the liquid speedily

becomes decolorized, and a black phosphide of copper, with a semi-metallic lustre, is formed. It is not soluble in hydrochloric acid, but if thrown into a solution of potassic cyanide is decomposed rapidly without the application of heat, bubbles of spontaneously inflammable phosphuretted hydrogen being disengaged. When heated to redness, it gives off phosphorus, and becomes converted into *hexacupric diphosphide*, Cu_6P_2. Abel prepares this phosphide of copper by passing the vapour of phosphorus over finely divided copper heated in a tube; he finds that this phosphide when mixed with potassic chlorate and gunpowder furnishes a powder of sufficient conducting powder for electricity, and at the same time possessed of the requisite inflammability to enable it to be employed with great advantage as a detonating fuse for firing ordnance by magneto-electric currents.

(1050) **CUPRIC SULPHATE,** *Sulphate of copper,* or *Blue vitriol;* $CuSO_4.5OH_2 = 159{\cdot}4 + 90$; *Density, anhydr.* 3·631; *cryst.* 2·254; *Comp. in* 100 *parts cryst.*, CuO, 31·84; SO_3, 32·07; OH_2, 36·09.—This salt is manufactured on a large scale, by boiling copper in an iron pot with sulphuric acid, diluted with half its bulk of water: the acid is decomposed, and the copper is oxidized at its expense whilst the salt is precipitated. It may also be formed from an artificial sulphide of copper, by roasting it with free access of air, and lixiviating the roasted mass to dissolve the sulphate thus produced: the heat must be moderate, or else the sulphate will be decomposed during the roasting. If copper pyrites be used instead of the artificial sulphide, the salt will contain a large quantity of ferrous sulphate, which cannot be separated by crystallization; for although cupric sulphate does not crystallize alone with more than $5OH_2$, yet when mixed with ferrous sulphate, it, like this salt, assumes $7OH_2$, and then is isomorphous with the ferrous salt. The only plan in such a case is to ignite the mixed sulphates feebly: the iron salt parts with its acid at a lower temperature than the copper salt, and by a second solution the iron is separated in the form of an insoluble oxide. Cupric sulphate is also obtained in considerable quantity as a secondary product in the refining of silver (1141): the silver is precipitated from the solution of its sulphate in the metallic form, by plates of copper, and a pure cupric sulphate is thus produced.

Large quantities of cupric sulphate are used in calico-printing, and it is the salt from which most of the pigments of copper are prepared. It is soluble in four times its weight of water at 15° (59° F.), and crystallizes in beautiful blue crystals of the doubly oblique-rhombic form. The powdered crystals absorb hydrochloric acid gas rapidly with evolution of heat, and furnish a deliquescent mass. When cupric sulphate is heated at 100° (212° F.) it loses $4OH_2$, and at a temperature of 200° (392° F.) the salt becomes anhydrous, and assumes the appearance of a

white powder, which becomes blue on the addition of water. The act of combination with water is attended with a hissing noise, owing to the great rise of temperature which attends the action; a considerable evolution of heat also attends the combination of the compound, $CuSO_4.OH_2$, with water. Cupric sulphate is insoluble in alcohol. When heated to bright redness, the elements of sulphuric anhydride are expelled, and cupric oxide is left.

Cupric sulphate forms double salts with the sulphates of potassium and ammonium; they are easily obtained by mixing solutions of their constituent salts in equivalent proportions, and allowing the mixture to crystallize. The potassium salt is composed of $CuSO_4.K_2SO_4.6OH_2$; *density*, 2·244; the ammonium salt of $CuSO_4.(NH_4)_2SO_4.6OH_2$; *density*, 1·891. According to Graham, a hot saturated solution of potassic cupric sulphate deposits a remarkable basic double salt, the composition of which may be represented by the formula, $K_2SO_4.3CuSO_4.CuO.4OH_2$.

Anhydrous cupric sulphate absorbs dry ammoniacal gas; the compound consists of $CuSO_4.5NH_3$ (H. Rose). If ammonia be added in excess to a solution of cupric sulphate, the liquid on evaporation yields dark blue crystals ($CuSO_4.4NH_3.OH_2$; Berzelius); the salt, when heated to 150° (302° F.), becomes green, losing two molecules of ammonia and one of water.

Basic Sulphates of Copper.—If a solution of 1 molecule of cupric sulphate is boiled with less than 1 molecule of hydrated cupric oxide, a green insoluble *tribasic sulphate*, $CuSO_4.2CuH_2O_2$, is formed. *Brochantite* is a native basic sulphate of the metal, composed of $CuSO_4.3CuH_2O_2$; and Denham Smith obtained a basic salt consisting of $CuSO_4.4CuO.6OH_2$. Many other basic sulphates have been examined.

(1051) **CUPRIC NITRATE**, $Cu2NO_3.6OH_2$, is easily made by dissolving copper in nitric acid: it forms a beautiful blue deliquescent salt which crystallizes in rhomboidal prisms. At temperatures above 15° (59° F.) it crystallizes with $3OH_2$ in deliquescent needles of density 2·047, which are very soluble in alcohol. It is decomposed by a moderate heat with formation of a green *basic nitrate* [$Cu2NO_3.3CuH_2O_2$; Gerhardt], which is insoluble, but if the heat be increased, it is entirely converted into the black oxide, the nitric anhydride being expelled. It is this basic nitrate which is formed when cupric oxide is treated with monohydrated nitric acid, although the acid may be in considerable excess. If a few crystals of cupric nitrate are moistened and wrapped up in tinfoil they act violently upon the metal, and rapidly convert it into stannic oxide with emission of sparks.

Several basic cupric *phosphates* are found native in small quantities.

(1052) **CARBONATES OF COPPER.**—All attempts to procure the neutral cupric carbonate have hitherto failed. A *hydrated*

oxycarbonate, called *chessylite,* $CuH_2O_2.2CuCO_3$ (*density* 3·8), forms a beautiful blue mineral, which crystallizes in oblique rhombic prisms. But the most abundant of the carbonates of copper is the hydrated dibasic carbonate, or *malachite,* $CuH_2O_2.CuCO_3$; (*density* from 3·7 to 4·0). It forms a very hard mineral of a silky lustre, and a beautiful green colour; it is susceptible of a high polish, by which its concentric and often beautifully veined structure is advantageously displayed. It is often employed for ornamental purposes. Malachite is occasionally found in oblique prisms. Both the blue and the green carbonate are abundant in the copper ore from Australia. A green precipitate, sometimes used as a pigment, which has the same composition as malachite, and is known as *mineral green,* may be obtained by mixing hot solutions of cupric sulphate or nitrate and sodic carbonate. If the solutions be mixed cold, a pale blue voluminous precipitate is formed, which, according to Brunner, is the same compound, with an additional molecule of water, $CuO.2OH_2.CuCO_3$. By boiling the precipitated carbonate, it becomes first green and then black, losing nearly all its water, and carbonic acid. When the basic carbonate is treated with an aqueous solution of carbonic acid, saturated under a pressure of five or six atmospheres, a greenish solution is obtained, and a green crystalline powder is left having the same composition as malachite. A double carbonate of potassium and copper, $K_2CO_3.4CuCO_3.CuO.10OH_2$, may be obtained by digesting the green carbonate in a solution of hydric potassic carbonate: it is deposited in blue crystals by spontaneous evaporation. Similar salts may be formed with sodium and ammonium.

(1053) **Characters of the Salts of Copper.**—1. *Salts of the suboxide,* or *Cuprous salts.*—They are nearly all insoluble in water, but soluble in hydrochloric acid; in this form they absorb oxygen rapidly, and are converted into salts of the black oxide. They are unimportant, and have been but little studied; one of their most remarkable properties is their power when in solution in hydrochloric acid of absorbing carbonic oxide, with which they form a crystalline compound.

2. *Salts of the black oxide,* or *Cupric salts.*—Most of these salts of copper have a green or a blue colour when hydrated, but they are white when anhydrous; they are almost all soluble. They have a strong, disagreeable metallic taste, and act as poisons in the animal system, producing violent and irrepressible vomiting and purging, followed by exhaustion and death. They form an insoluble compound with albumin, which is nearly inert; raw

whites of eggs should therefore be administered in cases of poisoning suspected to be occasioned by this metal. Milk or sugar mixed with iron filings, by reducing the cupric to cuprous salts, or to the metallic state, are also valuable remedies.

The cupric salts are easily recognized when in solution; although neutral in composition they redden litmus. *Potassic* and *sodic hydrates* give in their solutions a pale blue voluminous precipitate of hydrated basic salt; an excess of the alkali does not dissolve it, but converts it into a blue hydrated oxide, which becomes black and anhydrous when the liquid is boiled with it. If sugar or tartaric acid, or certain other organic substances be present, the blue precipitate is redissolved by an excess of the alkaline liquid, and forms a blue solution. *Ammonia* gives a similar precipitate, but an excess of the alkali redissolves it, forming a deep blue solution, which is very characteristic. *Potassic* or *sodic carbonate* gives a pale blue hydrated basic carbonate, which becomes gradually converted into the black oxide when boiled in the liquid with excess of the alkaline carbonate. *Ammonic sesquicarbonate* also gives a blue precipitate, but redissolves it if added in excess, forming an intensely blue solution. *Potassic ferrocyanide* yields a bulky brown precipitate, insoluble in hydrochloric acid, but soluble in ammonia, which leaves it unaltered on evaporation. *Sulphuretted hydrogen* gives a brownish-black hydrated sulphide, even in acid solutions. The last two characters distinguish the salts of copper from those of nickel, which also form a blue solution with ammonia. Cupric sulphide is almost insoluble in ammonia, and in ammonic hydric sulphide, but is dissolved by potassic cyanide. Another characteristic and very delicate test of the presence of copper is afforded by the action of a polished plate of *iron*, which in a feebly acid solution, is speedily covered with a red deposit of metallic copper. *Zinc* precipitates copper in the form of a black powder, which assumes a metallic lustre under the burnisher. If a salt of copper be heated with sodic carbonate on charcoal *before the blowpipe* in the reducing flame, a bead of metallic copper is obtained, which may be recognized by its colour and its malleability. Most copper salts when heated on platinum wire communicate an intense green colour to the oxidizing flame.

In cases in which the presence of copper is suspected in admixture with organic matters, as in the contents of the stomach, where it is supposed to have acted as a poison, the material must be reduced to dryness, and incinerated in an earthen crucible. The ash is then to be treated with nitric acid, and the liquid tested with ammonia, with potassic ferrocyanide, and with a steel needle. The copper-coloured deposit on the steel may be further identified by

placing it in a narrow tube with a few drops of ammonia, which will become blue in the course of 24 hours if copper be present (Taylor).

The salts of copper have considerable tendency to form double salts, and basic salts of this metal may be obtained with various acids: those with sulphuric, nitric, carbonic, and acetic acids are the most important.

(1054) **Estimation of Copper.**—This is generally effected in the form of the black oxide, 100 parts of which correspond to 79·85 of the metal. If the solution contains no metal precipitable by potassic hydrate, an excess of solution of potash is added and the liquid is boiled; the precipitate is well washed with boiling water.

Pelouze (*Ann. Chim. Phys.*, 1846, [3], xvi. 426) has described a method of estimating the quantity of copper, by bringing it into solution with excess of ammonia, and ascertaining the quantity of a standard solution of disodic sulphide which is required to decolorize the liquid. The process is rapid, and admits of being applied in a large number of cases.

A still better method, according to E. O. Brown (*Jour. Chem. Soc.*, 1857, x. 65) consists in treating the solution of copper with one of potassic iodide; cuprous iodide, Cu_2I_2, is thus formed, and iodine is set at liberty: the amount of the latter is determined by a standard solution of sodic thiosulphate (hyposulphite of soda): in order to effect the operation, a weighed quantity of the ore is dissolved in nitric acid, boiled until red fumes cease to escape, and the nitrous acid is all expelled: it is then diluted with water, and sodic carbonate added until a slight permanent precipitate is formed. Acetic acid in excess is added, and afterwards an excess of potassic iodide and a few drops of a solution of starch. The quantity of iodine thus set free is then estimated by the number of divisions of a standard solution of sodic thiosulphate required to convert the iodine into hydriodic acid, a point which admits of most accurate determination by the disappearance of the blue tinge. The solution of thiosulphate is graduated by dissolving 0·5 gram of pure copper in nitric acid, and subjecting it to a series of operations exactly corresponding to those performed upon the ore, noting the number of divisions of the standard solution consumed in neutralizing the amount of iodine set free.

The copper may also be estimated as cuprous sulphocyanate, after rendering the solution as free from nitric acid as possible, by reducing it with sulphurous acid, and precipitating with potassic sulphocyanate; the precipitate contains 52·5 per cent. of copper. This is an excellent method of separation from zinc, nickel, cobalt, and manganese.

It may also be estimated by precipitation in the metallic state by electricity: the liquid containing the copper is poured into a platinum dish which is made the negative pole of a small battery, the positive electrode being a piece of platinum wire supported in the liquid. When the precipitation is complete the dish is washed out and dried *in vacuo* over sulphuric acid. The increase in weight of the dish gives the quantity of copper in the solution.

Copper may be readily separated from the metals of the first five groups, with the exception of cadmium, by the action of sulphuretted hydrogen. The precipitated cupric sulphide must be washed with water containing sulphuretted hydrogen in solution,

in order to prevent its oxidation on the filter. The precipitate must be detached from the filter, redissolved in nitric acid (815), and the cupric oxide precipitated by means of potassic hydrate.

If cadmium be present, Stromeyer directs that the precipitate of the mixed sulphides, obtained by passing sulphuretted hydrogen through the liquid, be redissolved in nitric acid, and precipitated by an excess of ammonic sesquicarbonate, which, if left to stand for a few hours, dissolves the copper, but leaves the cadmium in the form of carbonate.

The separation of copper from bismuth may be effected by means of ammonic sesquicarbonate, as directed for cadmium.

The other metals of the sixth group are separated by precipitating them with the copper as sulphides, and then digesting the mixed sulphides with a solution of potassic hydric sulphide (ammonic hydric sulphide dissolves traces of copper); the cupric sulphide alone remains undissolved.

§ II. LEAD: Pb″=207.

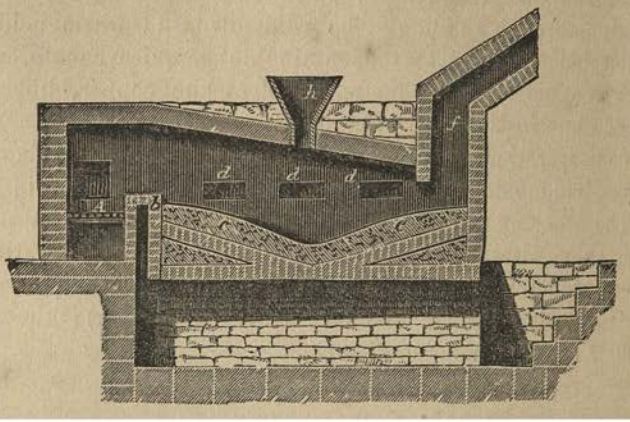
(1055) **LEAD** (Plumbum): *Density*, 11·38; *Fusing-pt.* 325° (617° F.); *usually Dyad, as in* $PbCl_2$; *sometimes Tetrad, as in* $Pb(C_2H_5)_4$.—Almost all the lead of commerce is obtained from galena, the native plumbic sulphide. It occurs, mixed with quartz, blende, pyrites, baric sulphate, and fluor-spar, in veins traversing the primitive rocks, and particularly in the clay-slate in Cornwall, and mountain limestone in Cumberland. Small quantities of plumbic carbonate and phosphate are frequently met with, but they are unimportant as ores of the metal. Galena always contains a small proportion of argentic sulphide; when the mineral is found in bold, well-characterized cubes, it is usually nearly pure. The proportion of silver in galena is liable to considerable variation; a mineral yielding 120 ounces of silver to the ton, or 0·36 per cent., is considered to be extremely rich. England and Spain afford the principal supply of this metal, about 65,000 tons of lead being anually raised in England, which furnish on the average 700,000 ounces of silver.

(1056) **Extraction of Lead from its Ores.**—After the lead ore has been raised to the surface, it undergoes a careful mechanical preparation, conducted upon the principles already explained (556); and having been thus freed to a great extent from its earthy impurities, it is ready for smelting.

If the galena be tolerably free from siliceous gangue, this operation is sufficiently simple. About 1½ ton of the dressed ore

is mixed with from a fortieth to a twentieth of its weight of lime, and is heated to dull redness in a reverberatory furnace, through which a strong current of air is passing. Fig. 362 exhibits a

FIG. 362.



section of the reducing furnace employed in Derbyshire. *A* is the fire-grate, *b* the bridge, *h* the hopper by which the charge is introduced: *c c*, the bed on which the ore is placed, sloping downwards towards a gutter in the centre, by which the melted metal is drawn off; *d, d, d,* are doors for working the charge and for admitting air, the draught of the furnace being completely under control by a damper placed in the flue *f*.

During the roasting, a large quantity of the sulphur burns off as sulphurous anhydride, and a portion of plumbic oxide is formed: another portion of the plumbic sulphide is converted into sulphate, and much of the ore still remains undecomposed. In the course of the operation, the mass is frequently stirred, and care is taken not to allow the temperature to rise sufficiently high to fuse it. When it is considered that the roasting has been carried far enough, the materials on the bed of the furnace are thoroughly mixed together, the furnace doors are closed, and the heat is suddenly raised. The plumbic oxide and sulphate then react upon the undecomposed sulphide of the metal; a large quantity of sulphurous anhydride is evolved, whilst metallic lead runs copiously from the mass. The successive stages of this operation may be traced as follows:—Two molecules of plumbic sulphide, by combining with 6 atoms of oxygen, furnish 2 molecules of plumbic oxide and 2 of sulphurous anhydride, as is exhibited by the equation: $2PbS + 3O_2 = 2PbO + 2SO_2$. If 1 molecule of galena unite with 4 atoms of oxygen, 1 molecule of plumbic sulphate is

formed: $PbS + 2O_2 = PbSO_4$. Both the plumbic oxide and sulphate, when heated with fresh sulphide of lead, are decomposed, metallic lead and sulphurous anhydride being in each case the result of the reaction. Two molecules of plumbic oxide and 1 of galena furnish 3 atoms of lead and 1 molecule of sulphurous anhydride: $2PbO + PbS = 3Pb + SO_2$. One molecule of plumbic sulphate, when heated with 1 of galena, yields 2 atoms of lead and 2 molecules of sulphurous anhydride: thus $PbS + PbSO_4 = 2Pb + 2SO_2$. During the roasting, a portion of plumbous sulphide, Pb_2S, is also produced: this substance forms a fusible matt, which flows from the furnace with the metallic lead, constituting a stratum which floats above the melted metal. This subsulphide is again returned to the furnace and roasted with fresh ore.

After the melted mass has been drawn off into cast-iron basins placed for its reception, a few spadefuls of lime to which a quantity of fluor-spar is sometimes added, are thrown into the furnace with a view to act upon the scoriæ which remain behind in considerable quantity: the lime decomposes the fusible plumbic silicate, liberates plumbic oxide, and forms a less fusible calcic silicate, and the fluor-spar forms a fusible compound with the calcic or baric sulphate, if either of them be present. The scoriæ usually contain an excess of plumbic oxide and sulphate: they are therefore mixed with coke or charcoal, and exposed to heat on the bed of the furnace, after the doors have been carefully closed: the plumbic oxide then becomes reduced by the carbon.

(1057) **Refining of Lead.**—Lead which contains antimony or tin is harder than the pure metal, and is subjected to a further operation, termed *improving*, in order to refine it. This consists simply in melting the lead, and heating it for a period, longer or shorter, as may be necessary, in a shallow cast-iron pan set in the bed of a reverberatory furnace; the antimony and tin being more oxidizable than the lead, are thus removed in the pellicle of oxide which is continually being formed. From time to time the workman takes out a small sample of the metal to examine the appearance which it presents on cooling. As soon as it exhibits a peculiar flaky crystalline appearance on the surface, the oxidation has been carried far enough; the metal is then run off and cast into pigs.

(1058) **Concentration of Silver in Lead by Pattinson's Process.**—Silver may be profitably extracted from lead, even when the quantity does not exceed from three to four ounces of silver to the ton, by a process introduced by Mr. Pattinson, of

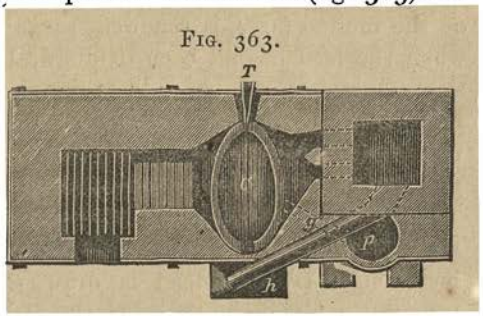
Newcastle. This gentleman observed that if melted argentiferous lead be briskly stirred during slow cooling, a portion of the metal solidifies first, in the form of crystalline grains, which sink to the bottom of the still fluid portion. These crystals consist of lead nearly free from silver, the fusing-point of the alloy of lead and silver being lower than that of pure lead. This observation is turned to account in the concentration of the argentiferous alloy. Eight or nine cast-iron pots, each capable of containing about five tons of melted lead, are arranged in a row, set in brickwork, and each provided with a separate fireplace underneath. A quantity of lead is introduced into the middle pot, and melted; the fire is then withdrawn, and the metal is briskly stirred by the workman whilst it cools: the crystals of lead subside as they form, and are removed at intervals by means of a large perforated iron ladle, and transferred to the next pot on the right hand. When about four-fifths of the metal have been thus removed in crystals, the concentrated argentiferous alloy is ladled out into the next pot on the left-hand side, and the empty pot is charged with a fresh portion of lead, which is subjected to a similar treatment. When the pot to the right and to the left has in this manner received a sufficient quantity either of poor or of argentiferous lead, it is subjected to a similar operation; the concentrated argentiferous portion being passed off continually to the next pot on the left, whilst the crystalline or poorer portion is handed over to the next pot on the right-hand side. The last pot to the left thus at length becomes filled with lead which may contain 300 ounces of silver to the ton (0·9 per cent.); it is not found advantageous to concentrate it beyond this point: the lead which accumulates in the last pot on the right-hand side does not contain more than half an ounce of silver in the ton. This poor lead is much improved in quality by the operations which it has undergone, and is at once cast into pigs for the market.

(1059) **Extraction of Silver from Lead by Cupellation.**—The rich argentiferous lead is now subjected to *cupellation*. This process is founded upon the circumstance that lead, if exposed at a high temperature to a current of air, absorbs oxygen rapidly, and is converted into a fusible oxide, whilst silver does not become oxidized, but is left behind in the metallic state. The litharge or plumbic oxide melts at a high temperature, and flows off the convex surface of the melted metal, and thus continually exposes a fresh surface of lead to the action of the air.

In England the cupellation is performed in a low-crowned

reverberatory furnace, the hearth of which is moveable. The hearth or *cupel* is shown in the plan of the furnace (fig. 363): it consists of a shallow oval basin, c, composed of a mixture of bone ash with fern or wood ashes; this mixture is slightly moistened, and beaten into an iron ring of about 4 feet in its long diameter, and 2 feet in the shorter (1·2 by 0·6 metre): the cupel is introduced into the furnace from beneath, and is supported by bricks, so that it can be readily removed and renewed,—an operation which is generally required once a week. When dry, the fire is lighted cautiously, and the lead introduced; a continual blast of air from a tuyère, T, is made to play over the surface of the melted metal; litharge is formed abundantly, and runs off through a gutter, *g*, into an iron pot, *p*, placed beneath the furnace for its reception; in front is a hood, *h*, for carrying off the fumes of oxide of lead which would otherwise escape and injure the workman. Fresh lead is added from time to time to supply the place of that which is oxidized; until at length a quantity of lead, originally amounting to about 5 tons, is reduced to between 2 and 3 cwt. This melted metal is withdrawn by making a hole through the bottom of the cupel; the aperture is afterwards closed with fresh bone ash, and another charge is proceeded with. When a quantity of rich lead sufficient to yield from 3000 to 5000 ounces of silver, or from 93 to 155 kilos. has thus been obtained, it is again placed in a cupel, and the last portions of lead are removed. It is found advantageous to effect this final purification of the concentrated silver lead separately, because in the last stages of the operation the litharge carries a good deal of silver down with it: these portions of litharge, therefore, on being reduced, are again subjected to the desilvering process.

Fig. 363.



The litharge from the first fusion is either sold as such, or it is reduced in a small reverberatory furnace with anthracite, or powdered coal. The porous cupels absorb a large quantity of litharge, and they, likewise, are passed through the furnace in order to extract the metal.

A very beautiful phenomenon, known as the *fulguration* of the metal, attends the removal of the last portions of lead from

the silver. During the earlier stages of the process, the film of plumbic oxide, which is constantly being formed over the surface of the melted mass, is renewed as rapidly as it is removed; but when the lead has all been oxidized, the film of litharge upon the silver becomes thinner and thinner as it flows off; it then exhibits a succession of the beautiful iridescent tints of Newton's rings: and at length the film of oxide suddenly disappears, and reveals the brilliant surface of the metallic silver beneath.

Lead is now often desilverized by means of zinc. The zinc is stirred into the melted argentiferous lead, and after the zinc scum has formed, the poor lead is drawn off and the zinc it contains removed as oxide by exposing the metal heated to redness to the action of superheated steam. The argentiferous zinc scum is likewise treated with superheated steam, when it yields a very rich lead, and zinc oxide mixed with the silver lead alloy. Sometimes this mixture of oxide and alloy is treated with hydrochloric acid to remove the zinc, at others it is treated with the rich lead during cupellation, using a very high temperature so that the zinc passes away with the slag.

In the Hartz the hearth of the cupellation furnace is fixed, and is made of brick, covered with marl, which is renewed after each operation, but the cover of the furnace is moveable. Karsten states that the advantage of this method is, that the litharge runs off more perfectly, and that there is less waste of silver from absorption into the cupel, and less expenditure of labour and fuel upon recovering the lead from the bottom of the furnace, which absorbs comparatively little litharge.

(1060) **Other Processes of Lead Smelting.**—In the North of England, the galena is smelted by a process somewhat different: the ore is first roasted, and then reduced in a small square blast furnace, or forge hearth,—dried peat being the fuel principally employed. This form of furnace is known as the *Scotch furnace.*

In some parts of the Hartz, where the ores are largely mixed with siliceous matters, the English method of smelting is not applicable, as the silica would combine with the oxide of lead, and form a fusible slag. It is found necessary in these cases to reduce the sulphide of lead by means of metallic iron, which is added in the form of granulated cast-iron, in the proportion of about 1 part of iron to 20 of pure galena. The fusion is performed in a small blast furnace, about 6 metres high and 0·9 m. across, or 20 feet high, and 3 feet across at the widest part.

These various furnace operations are attended by a continual disengagement of white fumes, which consist principally of plumbic oxide and sulphate, and are technically termed *froth of lead;* in this way nearly a seventh of the whole lead is volatilized. Independently of the waste thus occasioned, the fumes are highly deleterious; it is therefore of great importance to prevent as far as possible their diffusion through the air. It is stated that in the Hartz about $\frac{7}{10}$ of the volatilized portion is arrested by causing the gases from the furnaces to pass through a succession of condensing chambers, before they finally escape into the

air. At Allenheads, in Cumberland, a flue which ascends the side of a hill of three miles in length has been employed to condense these fumes.

(1061) **Properties of Lead.**—Lead is a bluish-white metal, so soft that it may easily be made to take impressions: it leaves a mark upon paper, and may be cut with the nail. It may be laminated into tolerably thin sheets, as well as drawn into wire; but in both ductility and tenacity it is low in the scale. It fuses at 325° (617° F.), Rudberg, or 327° (620° F.), Person, and may with some difficulty be obtained in cubic or octahedral crystals as it cools: the purer the lead the larger the crystals (Baker, quoted by Matthiessen). Lead contracts considerably at the moment of its solidification, and it is therefore not well adapted for castings. It appears to have the power, when melted, of dissolving a small quantity of plumbic oxide, by which the hardness of the metal is much increased; but its softness may be restored by keeping it melted under charcoal for some time, with occasional agitation. As a conductor of heat and electricity, it is inferior to many of the other metals.

At high temperatures, lead absorbs oxygen rapidly from the air; it undergoes partial volatilization, and emits white fumes of oxide. It is not acted upon by sulphuric or hydrochloric acid at ordinary temperatures, and but slightly even when boiled with them; but it is dissolved by nitric acid, with evolution of nitric oxide, especially when the acid is somewhat dilute. The vapours of acetic acid corrode it rapidly, and if carbonic acid be also present, convert it gradually into white lead. Green oak wood, from the quantity of acetic acid which it contains, should not be used in contact with lead for building purposes. The alkalies do not exercise any decided influence upon lead. Chlorine slowly converts the metal into chloride, but the film of this compound, which is formed on the surface, protects the metal beneath. In the presence of moisture, lead is corroded by calcic sulphate; hence in its application to architectural purposes, the contact of stucco or plaster with lead should be avoided.

The lead of commerce is often nearly pure. The purest specimens are the softest. Traces of tin, iron, copper, and silver, and sometimes of antimony and manganese, are the impurities which are most often observed. In order to obtain it perfectly pure, it should be reduced with black flux from the oxide left by igniting the pure nitrate or carbonate of the metal.

(1062) **Combined Action of Air and Water on Lead.**—The surface of a piece of lead when freshly cut presents a high metallic

lustre, but it soon tarnishes by exposure to the air, owing to the formation of a thin, closely adhering film of oxide, which protects the metal from further change. Lead undergoes no alteration in a perfectly dry atmosphere, and even when sealed up in a vessel of pure water, which has been boiled for some time to expel the air, the metal will retain its brilliancy for an indefinite period; but if it be exposed to the united action of air and *pure* water, it is powerfully corroded. As the result of this exposure the lead becomes oxidized at the surface, and the water dissolves the oxide of lead; this solution absorbs carbonic anhydride, a film of hydrated basic carbonate of lead, $PbH_2O_2.PbCO_3$, is deposited in silky scales, and a fresh portion of oxide is formed and dissolved by the water; thus a rapid corrosion of the metal takes place. This action is modified very materially by the presence of various salts in the water, even when the quantity of these salts does not exceed 3 or 4 grains in the gallon (43 to 57 mgrms. per litre). The corrosion is much increased by the chlorides and nitrates, and the presence of very minute quantities of the nitrites in water confers upon it a corrosive action on lead. Both nitrites and nitrates are often present in spring and river waters, owing to the decomposition of nitrogenous organic matter; and it is not improbable that the unexplained corrosive action of certain soft waters upon lead may be due to the presence of these salts, especially as ammonic nitrate or nitrite is almost invariably found in such water (Medlock). Small quantities of ammonia also favour the solution of the metal. On the other hand the corrosion is diminished by the sulphates, the phosphates, and the carbonates. Plumbic oxide, indeed, is scarcely soluble in water which contains these salts in solution. A solution of calcic carbonate in carbonic acid is especially remarkable for the preservative influence which it exerts, and as this latter is a very usual impurity in water, few spring waters act on the metal to any dangerous extent: the presence of carbonic acid in distilled water almost entirely prevents its action on lead. In these cases a film of insoluble plumbic carbonate is formed upon the surface, and the metal beneath is protected from further injury. The action of water on lead is a matter of great importance in its sanitary bearings, on account of the extensive employment of this metal in cisterns and pipes for the storage and supply of water. Rain water, as collected from the roofs of houses, is for the most part sufficiently impure, especially in large towns, to prevent its action upon the metal. Of all the salts of lead, the hydrated basic carbonate is the least soluble, pure water not taking up

more than 1 part in 4 millions, or about a sixtieth of a grain per gallon. If a solution of plumbic oxide in distilled water containing 60 or 70 milligrams per litre, or about 4 or 5 grains to the gallon, be exposed to the air, it soon becomes filled with silky crystals of the hydrated basic carbonate, owing to the absorption of carbonic anhydride; and in a few hours the water does not contain more than $\frac{1}{4,000,000}$ of its weight of the metal in solution. Water highly charged with carbonic acid may nevertheless dissolve lead to a dangerous extent, owing to the solubility of plumbic carbonate in excess of carbonic acid; when water thus impregnated with lead is boiled, the gas is expelled, and the carbonate subsides. Sometimes, as in the soft lake waters of Scotland, the presence of a little vegetable matter acts as a preservative agent by combining with a portion of oxide of lead, and forming an insoluble and closely adhering natural pigment which lines the pipes and cisterns. So general, however, is the action of water upon lead, that it is rare to find any that has been kept in cisterns of this metal perfectly free from all traces of it. Slate cisterns are therefore greatly to be preferred to leaden ones. Lead immersed in sea water becomes covered with an insoluble lead compound, but the lead is not dissolved.

(1063) **Uses of Lead.**—From its softness, fusibility, durability, and the ease with which it can be worked, lead is applied to a multiplicity of purposes. The reception chambers in the manufacture of sulphuric acid are lined with it. It forms the ordinary material for cisterns, waterpipes, and gutters, and is frequently employed in covering the roofs of houses, and large buildings. Various compounds of lead are also employed in the arts. The red oxide is largely used in the manufacture of flint-glass. The carbonates, the oxychlorides, and the chromates are extensively employed as pigments.

(1064) **Alloys of Lead.**—The alloys of lead are numerous and important. Shot for fowling-pieces is an alloy of lead with a small proportion of arsenic, which hardens it and facilitates its granulation into globules; the quantity of arsenic varies with the purity and softness of the lead: usually it requires from 3 to 8 parts in 1000. The common white arsenic of the shops is added to the lead, melted in a covered vessel; the arsenious anhydride is reduced by the lead, and the oxide of lead thus formed rises as a film to the surface of the alloy. Sonnenschein observed an alloy of iron and lead, $FePb_2$, which had been accidentally formed in a blast furnace, in acicular feathery

crystals; it was yellow, harder than lead, and of density, 10·36; it contained 11·14 per cent. of iron.

When lead is alloyed with about one-third of its weight of antimony, it forms *type metal:* a superior variety of type consists of 1 part of antimony, 1 of tin, and 2 of lead; it is harder and tougher than the common alloy used for this purpose. Both the alloys are sufficiently fusible to allow of being readily cast; they expand at the moment of solidification, and copy the mould accurately; they are hard enough to bear the action of the press, and yet not so hard as to cut the paper. Alloys of lead containing about 1 per cent. of antimony or copper resist the action of sulphuric acid better than pure lead. The ordinary *fusible metal* contains lead, as do the various compounds called pewter, Britannia metal, and Queen's metal. The solder used by tinplate workers and plumbers is a mixture of lead and tin (924). When lead is melted with zinc, a white, hard ductile alloy is formed; but the two metals separate into two distinct layers, if the fused mass be left to cool slowly. *Pot metal* is an alloy of lead and copper, obtained by throwing lumps of copper into red-hot melted lead (Brande): it is of a grey colour, brittle, and granular.

(1065) **PLUMBIC CHLORIDE**, or *Chloride of lead*, $PbCl_2 = 278$; (*Density*, 5·8; *Comp. in* 100 *parts*, Pb, 74·46; Cl, 25·54), is best prepared by precipitating a solution of plumbic nitrate by the addition of hydrochloric acid, or of a solution of sodic chloride; it is a sparingly soluble, heavy white precipitate. It is soluble in about 33 parts of boiling water, but less so in dilute hydrochloric acid; the concentrated acid, however, dissolves it readily, and deposits it in long, delicate, six-sided needles. It is also soluble to a considerable extent in ammonium acetate, so that no precipitate is produced by hydrochloric acid in a solution of lead acetate containing much ammonium acetate. Glycerin dissolves about 2 per cent. of its weight of the chloride. Plumbic chloride is easily fusible into a semi-transparent, horny, sectile mass, which is volatile at a high temperature. If fused in contact with the air until no more fumes arise, it is converted into an oxychloride, $PbO.PbCl_2$. The alkalies at first convert it into an oxychloride, and if the action be prolonged, into pure oxide.

Oxychlorides of Lead.—The chloride combines with oxide of lead in several proportions. One of these forms a white, translucent, fusible, colourless mineral, $2PbO.PbCl_2$, *mendipite*, which is found in the Mendip Hills crystallized in right rhombic prisms. Pattinson's white oxychloride of lead, $PbO.PbCl_2$, is prepared by

grinding galena in a closed chert mill with concentrated hydrochloric acid : sulphuretted hydrogen is liberated in large quantity, and the sparingly soluble plumbic chloride is first washed with common water, and chalk added to neutralize every trace of the acid : it is then dissolved in hot distilled water, and precipitated by the addition of lime-water in quantity just sufficient to remove half the chlorine ; $CaO + 2PbCl_2 = CaCl_2 + PbO.PbCl_2$. This oxychloride is used to some extent as a pigment instead of white lead. Another oxychloride, $PbCl_2.7PbO$, is a pigment of some importance, known under the name of *patent yellow*, or *Turner's yellow* ; it forms a very fusible compound of a bright yellow colour, which may be obtained by heating together 1 part of sal ammoniac and 10 parts of litharge.

When an acid solution of plumbic chloride is precipitated by a current of sulphuretted hydrogen, the precipitate which is first formed is of a bright red colour, but by the further action of the gas it becomes black, and furnishes plumbic sulphide : the red compound is a *chlorosulphide* of lead, $3PbS.2PbCl_2$.

(1066) **PLUMBIC BROMIDE**, or *Bromide of lead*, $PbBr_2 = 367$ (*density* 6·63), is white, sparingly soluble, and fusible at a red heat.

(1067) **PLUMBIC IODIDE**, or *Iodide of lead*, $PbI_2 = 461$; *Density*, 6·384.—This is easily obtained by precipitating a solution of plumbic nitrate or acetate by one of potassic iodide : it is thrown down as a bright yellow powder, sparingly soluble in cold water, but more soluble in hot water ; the solution as it cools deposits beautiful golden-yellow spangles of a silky lustre ; they may be fused by a moderate heat. Plumbic iodide, suspended in water, is decomposed by sulphurous anhydride, plumbic sulphite and hydriodic acid being produced.

Plumbic iodide forms double salts with the iodides of the alkali-metals. Several oxyiodides of lead have also been prepared and examined.

A remarkable compound of oxyiodide of lead with carbonate of lead, $Pb_2OI_4.4PbCO_3$, of a blue colour, may be obtained by precipitating the tribasic plumbic acetate with a mixture of potassic tri-iodide (KI_3) and potassic carbonate.

Plumbic Fluoride, or *Fluoride of lead*, PbF_2, is white, insoluble, and fusible.

(1068) **OXIDES OF LEAD.**—Lead forms four oxides ;—an unimportant black suboxide, Pb_2O, obtained by heating the oxalate at about 320° (608 F.), in a glass retort. A protoxide, PbO, from which the ordinary salts of the metal are formed ; a dioxide, PbO_2, which is insoluble in acids ; and red lead which is a compound of the two oxides last mentioned, usually in the proportions indicated by the formula, $2PbO.PbO_2$.

(1069) **PLUMBIC OXIDE**, *Lead oxide*, or *Protoxide of lead*, PbO = 223; *Density*, 9·2 to 9·5; *Comp. in* 100 *parts*, Pb, 92·83; O, 7·17.—This oxide is well known under the name of *litharge*. Its colour varies according to the mode of its preparation. It is usually obtained on a large scale by the oxidation of lead in a current of air, in which case it forms a scaly mass, which, if of a yellow colour, is commonly termed 'litharge of silver;' if redder, it is termed 'litharge of gold.' The former is the purer, as the red colour is due in many cases to the presence of a small quantity of minium. If the oxidation be effected at a temperature below that required for the fusion of the oxide, a yellow powder termed *massicot* is obtained. Common litharge, when reduced to a fine powder, also has a dull yellow colour; when heated, it assumes a brown-red hue, which disappears again as it cools.

If a hot solution of sodic hydrate, density 1·42, be saturated with litharge, the oxide is deposited, as the liquid cools, in beautiful, anhydrous, rose-coloured crystals. If the solution of plumbic oxide in sodic hydrate be allowed to evaporate spontaneously by exposure to the air, the alkali gradually absorbs carbonic anhydride, and the oxide is deposited in transparent, anhydrous, dodecahedral crystals.

If the salt of lead be precipitated by the addition of an alkaline hydrate in slight excess, the oxide of lead is precipitated in the form of a white hydrate, $2PbO.OH_2$. Another hydrate, $3PbO.OH_2$, may be obtained in groups of transparent octahedra, or of four-sided prisms mixed with anhydrous crystals, by precipitating a solution of tribasic plumbic acetate by an excess of ammonia, at a temperature of 30° (86° F.).

Both litharge and the hydrated oxide of lead absorb carbonic anhydride slowly from the atmosphere.

Plumbic oxide fuses at a heat above redness, and crystallizes on cooling in semi-transparent scales. At a high temperature it combines rapidly with the earths and with silica, speedily destroying and penetrating the crucibles in which it is melted. It should not be fused in platinum crucibles, since it becomes decomposed into the dioxide, and metallic lead; the latter attacking and spoiling the crucible. The protoxide is slightly soluble in water, to which it communicates an alkaline reaction; the solution absorbs carbonic anhydride rapidly from the air, and mere filtration in many cases causes the deposition of a large portion of the oxide in the form of hydrated basic carbonate: the presence of a very small quantity of saline matter diminishes or prevents the solution of the oxide.

Oxide of lead is soluble in solutions of the alkaline hydrates; indeed it forms compounds with the alkalies and alkaline earths, which have been obtained in crystals; they are, however, decom-

posed by simple exposure to the atmosphere, owing to the absorption of carbonic anhydride. The solution of the oxide in lime-water is sometimes used as a hair-dye: the lime softens and partially decomposes the hair, and the lead of the oxide, combining with the sulphur of the hair, forms plumbic sulphide, which stains the hair of a permanent black. Litharge is in continual requisition by the assayer as a flux; it also enters largely into the composition of the glaze of common earthenware. A mixture of 1 part of massicot with 8 or 10 of brick-dust, made into a paste with linseed oil, forms *Dhil mastic*: it sets exceedingly hard, and is frequently employed to repair defects in stone facings; the stone should be moistened before applying the mastic.

Plumbic oxide is a powerful base. It has a strong tendency to form basic salts; those which it yields with acetic acid, and some of those with nitric acid, are soluble: they exert a strongly alkaline reaction upon test-paper, and absorb carbonic anhydride with avidity. Indeed, owing to the very sparing solubility of the basic carbonate of lead, a solution of a basic salt of lead is a most delicate test for the presence of carbonic acid, either in a gas or in distilled water; a mere trace of carbonic acid occasions the formation of the peculiar, silky, crystalline precipitate which characterizes the basic hydrated plumbic carbonate.

(1070) **MINIUM, or RED LEAD** (*Density* about 9·08), is a compound of protoxide of lead with the dioxide and occasionally occurs native. It was obtained by Berzelius as $PbO.PbO_2$, but its most usual composition is represented by the formula, $2PbO.PbO_2$, although well crystallized samples have been formed, which consisted of $3PbO.PbO_2$. All these compounds possess a brilliant red colour. If the latter two be treated with a solution of potassic hydrate, or with one of normal plumbic acetate, the excess of plumbic oxide may be dissolved out, and the compound, $PbO.PbO_2$, is left.

Red lead is obtained by heating metallic lead, so as first to procure the protoxide or massicot, keeping the temperature below the fusing-point of the oxide; the oxide so obtained is finely levigated in water, and the particles which are held in suspension are allowed to subside, dried, and exposed, in iron trays, to a heat of about 320° (608 F.), in a reverberatory furnace; oxygen is then gradually absorbed. If white lead is submitted to a similar roasting, the carbonic anhydride is expelled, leaving protoxide of lead, which is converted into minium of very fine quality by the gradual absorption of oxygen. The principal use of red lead is in the manufacture of flint-glass. Much

care is required in the preparation of minium for this purpose: it is necessary that it should be free from the oxides of other metals, which would impart colour to the glass. In the oxidation of the lead, which constitutes the first stage in the preparation of red lead, the metals which are more oxidizable than lead are removed with the first portions of oxide; whilst the copper and silver accumulate in the portions of oxide which are produced last. The intermediate stage of the operation is therefore that which furnishes the purest oxide. Minium is better suited to the glass-maker than litharge, because the excess of oxygen burns off any combustible matter which may accidentally be present, and converts the ferrous into ferric oxide. Red lead is also used for colouring the inferior kinds of red sealing-wax, and for paper-staining.

If minium is exposed to a high temperature it is decomposed, oxygen is evolved, and the protoxide of lead remains. Minium is insoluble in the acids, but it is decomposed by many of them, especially by nitric acid; a salt of the protoxide is formed, and the brown dioxide remains behind.

(1071) **PLUMBIC DIOXIDE**, or *Peroxide of lead*; PbO_2= 239; *Density*, 9·45; *Comp. in* 100 *parts*, Pb, 86·61; O, 13·39.—This compound is occasionally found native in iron-black, brilliant, hexahedral prisms, forming *heavy lead ore*. It is usually prepared by levigating minium very finely, and digesting the powder in boiling nitric acid, diluted with 4 or 5 times its bulk of water; the residue is washed with fresh nitric acid, and then with water, until everything soluble is removed. It may also be obtained by fusing at a gentle heat a mixture of 4 parts of litharge in fine powder, with 1 part of potassic chlorate and 8 parts of nitre, and washing the product with water. Wöhler prepares the dioxide by passing a current of chlorine through the magma obtained by mixing a solution of 4 parts of plumbic acetate with a solution of 3 parts of crystallized sodic carbonate: the plumbic carbonate, which becomes gradually but completely converted into dioxide, must be thoroughly washed; in this reaction sodic chloride is formed, and acetic and carbonic acids are set free:

$$Pb2C_2H_3O_2 + Na_2CO_3 + Cl_2 + 2OH_2 = PbO_2 + 2HC_2H_3O_2 + 2NaCl + H_2CO_3.$$

Various other oxidizing agents may be employed to convert the plumbic protoxide into dioxide: *e.g.* plumbic acetate when

heated with a solution of bleaching-powder yields the dioxide in crystals.

Plumbic dioxide is insoluble in water and in acids; when heated it is converted into the protoxide with disengagement of oxygen; sulphurous anhydride instantly decomposes it, forming plumbic sulphate; $PbO_2+SO_2=PbSO_4$; hence it is frequently employed in the laboratory to absorb sulphurous anhydride when mixed with other gases.

If digested in a solution of ammonia, or subjected to a current of the gas, mutual decomposition occurs; water, ammonic nitrate, and plumbic oxide are formed. Cold dilute hydrochloric acid dissolves this oxide, forming a rose-coloured solution, from which alkaline hydrates reprecipitate the dioxide; but if the acid be hot or concentrated, plumbic chloride is produced, and chlorine is set free. If the dioxide be mixed with a fifth of its weight of sulphur, the mixture takes fire by friction, sulphurous anhydride and plumbic sulphide being produced. Plumbic dioxide appears to possess feebly acid properties. By fusing the pure dioxide with excess of potassic or sodic hydrate, in a silver crucible, and dissolving the residue in a small quantity of hot water, crystals of potassic or sodic *plumbate* are formed as the solution cools: potassic plumbate consists of $K_2PbO_3.3OH_2$ (Fremy). Pure water decomposes these compounds, and the plumbic dioxide subsides. Like the peroxides of silver and manganese, plumbic peroxide is a conductor of electricity, and is formed at the zincode of the battery when aqueous solutions of the ordinary plumbic salts are decomposed by the voltaic current.

(1072) **SULPHIDES OF LEAD.**—The most important of these is the protosulphide, PbS, the *galena* of mineralogists. Besides this a subsulphide, Pb_3S, is formed as the *lead matt* in reducing galena; and a red persulphide is also obtainable, although its composition is not accurately known. This persulphide is formed on adding a solution of a persulphide of one of the alkali-metals to a solution of a salt of lead: it is quickly resolved in the liquid into protosulphide of lead and free sulphur.

(1073) **PLUMBIC SULPHIDE,** *Protosulphide of lead,* or *Galena,* PbS=239; *Density,* 7·59; *Comp. in* 100 *parts,* Pb, 86·61; S, 13·39.—Galena is an abundant mineral, and forms the principal ore of lead: it is a brittle substance, and is found crystallized, more or less distinctly, in cubes of a deep leaden colour and strong metallic lustre: it almost invariably contains silver, which may sometimes be observed in the metallic state penetrating the mass in slender filaments. Plumbic sulphide may be formed artificially by fusing lead with sulphur; or it may be precipitated as a hydrate by treating any of its salts, either in solution or in suspension in water, with sulphuretted hydrogen: if the solution be sufficiently acidulated with nitric acid, the precipitate is crystalline, consisting of microscopic cubes resembling galena. When

plumbic sulphide is fused with potassic carbonate (6 parts) and sulphur (6 parts) in a covered crucible, a greyish mass is obtained on cooling, through which small crystals of plumbic sulphide are disseminated. Plumbic sulphide requires a full red heat for its fusion, and at the same time undergoes partial volatilization. When heated in closed vessels, part of the sulphur is expelled, and a *subsulphide*, or *plumbous sulphide*, Pb_2S, is left: this subsulphide is formed on the large scale in the process for reducing galena; it is more fusible than the protosulphide, and may be melted at a high temperature without undergoing decomposition; but if it be heated only to the point at which it begins to soften, the subsulphide is decomposed, and metallic lead melts out, leaving the less fusible protosulphide. Galena, when heated in contact with air, is oxidized, part of the sulphur burns off, and a mixture of plumbic oxide and sulphate is formed. Nitric acid and aqua regia decompose it, converting it into sulphate: hydrochloric acid acts upon it but slowly in the cold, but at a boiling temperature it decomposes it freely with evolution of sulphuretted hydrogen. When this sulphide is fused with lime or with the hydrated alkalies, metallic lead is obtained. If heated with oxide of lead or iron, it is reduced with liberation of sulphurous anhydride. When heated with a small quantity of nitre a similar result is obtained. When plumbic sulphide is heated with metallic iron it is decomposed, sulphide of iron and metallic lead being the result; advantage is taken of this fact in the assay of galena: 10 grams of the powdered ore are mixed with 15 grams of black flux, 3 or 4 wrought-iron nails are placed in a Cornish crucible with their heads downwards, the mixture is introduced, and covered with a small quantity of fused and powdered borax. It is heated to full redness for 10 minutes: the nails are withdrawn, and, when cold, the crucible is broken, and the button of metallic lead is weighed. The Cornish assayers usually employ 200 grains of the ore in each trial.

(1074) **SELENIDE OF LEAD**, PbSe, occurs native as *clausthalite* in lead grey masses of density 7·0—8·8; it is also formed with incandescence when selenium and lead are heated together. Cold nitric acid decomposes it, dissolving the lead and leaving red selenium.

(1075) **PLUMBIC SULPHATE**, or *Sulphate of lead;* $PbSO_4$ = 303; *Density*, 6·30; *Comp. in* 100 *parts*, PbO, 73·6; SO_3, 26·4.—This compound occurs native in white prismatic or octahedral crystals; it is also found in combination with plumbic carbonate. When prepared artificially, it forms a white powder, slightly

soluble in nitric acid, freely so in a solution of ammonic acetate of density 1·060, or upwards, and in a strong solution of sodic acetate. An excess of sulphuric acid, however, throws down nearly the whole of the lead as sulphate from the acetic solution. The other salts of ammonium also possess the property of dissolving plumbic sulphate, but to a smaller extent: they form double salts with plumbic sulphate, and these compounds are slightly soluble. The sulphate is also readily decomposed and dissolved by a cold saturated solution of sodic chloride (100 parts easily dissolving 1 of $PbSO_4$): on standing some time crystals of plumbic chloride are deposited: advantage has been taken of this property for extracting lead from its ores by a wet method. Plumbic sulphate is dissolved also, to some extent, by concentrated sulphuric acid, but it is insoluble in pure water. Hot hydrochloric acid likewise dissolves it sensibly, and deposits crystals of plumbic chloride on cooling, leaving a portion of free sulphuric acid in the solution. It may be obtained by adding sulphuric acid, or a solution of any sulphate, to a solution of one of the salts of lead. It is produced in large quantities as a secondary product during the preparation of aluminic acetate. Like all the insoluble compounds of lead, it is gradually decomposed by sulphuretted hydrogen; a black plumbic sulphide is formed, and the acid is set free. Before the blowpipe it yields metallic lead in the reducing flame, although it will bear a high temperature without decomposition when heated alone. Plumbic sulphate and sulphide when heated together decompose each other, as explained when speaking of the process of lead smelting (1056). The sulphate is reduced when heated with carbon, but the products vary with the proportion of carbon used, as may be seen by the annexed equations:

$$2PbSO_4 + C = 2PbO + CO_2 + 2SO_2;$$
$$PbSO_4 + C = Pb + CO_2 + SO_2;$$
$$PbSO_4 + 4C = PbS + 4CO.$$

(1076) **Plumbic Sulphite**, $PbSO_3$, is a white powder, insoluble in water, but soluble in acids with elimination of sulphurous acid: when heated it is partially decomposed, with evolution of sulphurous anhydride.

(1077) **NITRATES OF LEAD.**—Plumbic oxide forms several salts with nitric acid, viz., Pb_2NO_3; $Pb_2NO_3.PbH_2O_2$; $2(Pb_2NO_3.2PbO).3OH_2$; and $Pb_2NO_3.5PbO.OH_2$.

Plumbic Nitrate, or *Nitrate of lead*; $Pb_2NO_3 = 331$; *Density*, 4·40; *Comp. in 100 parts*, PbO, 67·37; N_2O_5, 32·63.—This, the normal nitrate, is easily prepared by dissolving litharge or metallic lead in an excess of nitric acid somewhat diluted: it crys-

tallizes in regular anhydrous octahedra, which are sometimes transparent, but more commonly milk-white and opaque. It is soluble in about 8 parts of cold water, is sparingly soluble in nitric acid, and insoluble in alcohol. If heated to redness, it decrepitates strongly, then fuses and is decomposed; oxygen and nitric peroxide, N_2O_4, are evolved (407), whilst plumbic oxide remains.

Caustic ammonia, if added to a solution of the nitrate, in quantity insufficient to combine with the whole of the acid, throws down a sparingly soluble *dibasic plumbic nitrate*, $Pb2NO_3.PbH_2O_2$. This salt may be also prepared by boiling the normal nitrate with litharge, or by precipitating a solution of plumbic nitrate with basic plumbic acetate. It is said to be deposited from its solution in hot water, in small, opaque, anhydrous crystals which decrepitate strongly when heated. The late Dr. Miller, however, stated that he always found it to crystallize in leaflets with OH_2, and this accords with Péligot's observation. By precipitating the nitrate with a slight excess of ammonia, a *tribasic nitrate* is formed, which falls as a white powder, containing $1\frac{1}{2}OH_2$; by adding a large excess of ammonia to the normal nitrate, a *hexanitrate* is formed; it also contains $1\frac{1}{2}OH_2$ (Berzelius).

(1078) **NITRITES OF LEAD.**—The action of metallic lead on a solution of normal plumbic nitrate is remarkable; the solution of the normal salt dissolves the metal without evolution of gas, whilst basic salts of the lower oxides of nitrogen are produced. Several of these compounds may be obtained; the composition of the basic salt varying according to the proportions of the normal nitrate and of the metal employed. When a solution of 331 parts, or 1 molecule of normal plumbic nitrate, is heated at about 60° (140° F.), with 207 parts or 1 atom of metallic lead, perfect solution takes place, and a salt having the formula $2PbNO_3.OH_2$ crystallizes on cooling, in yellow needles and plates; for $Pb2NO_3 + Pb = 2PbNO_3$. If $1\frac{1}{2}$ atoms of lead be employed instead of 1, another salt, composed of $4PbNO_3.3PbH_2O_2$, crystallizes in heavy orange-red needles. By boiling a very dilute solution of the nitrate with 2 atoms of lead for some time, a third salt, which is a *tetrabasic-nitrite of lead*, composed of $Pb2NO_2.3PbO.OH_2$ (Péligot), crystallizes in hard, rose-red, silky needles, which are but sparingly soluble in hot water, and still less so in cold: a normal plumbic nitrite, $Pb2NO_2$, may be formed by passing a current of carbonic anhydride through the solution of the basic nitrite just mentioned: a dibasic nitrite, $Pb2NO_2.PbH_2O_2$, as well as a tribasic nitrite, $Pb2NO_2.2PbO$, have also been formed (Bromeis).

(1079) **PHOSPHATES OF LEAD.**—The salts of lead give a white precipitate with the soluble salts of each modification of phosphoric acid; these phosphates are principally interesting as furnishing an easy means of obtaining these different acids, by suspending the corresponding salt in water, and decomposing it by means of a current of sulphuretted hydrogen. All the phosphates of lead are soluble in nitric acid. *Plumbic pyrophosphate*, $Pb_2P_2O_7$, when heated before the blowpipe furnishes a semi-transparent globule, which becomes remarkably crystalline on cooling. *Triplumbic diphosphate* occurs both massive, and crystal-

lized in six-sided prisms; the produce of a small mine at Wissembourg consists principally of this compound, mixed with plumbic carbonate. A *chlorophosphate of lead* called *pyromorphite*, $PbCl_2.3Pb_3 2PO_4$ (*density* 7·01), is found native in yellow six-sided prisms; it is readily fusible.

(1080) **Plumbic Borates and Silicates.**—*Boric anhydride* may be fused with plumbic oxide in all proportions; borate of lead enters into the composition of Faraday's optical glass. The *silicates of lead* enter largely into the formation of flint-glass. Silica and plumbic oxide may be fused together in almost all proportions; the larger the proportion of silica the less fusible is the compound, and the freer from colour: with an excess of oxide the glass is yellow.

(1081) **CARBONATES OF LEAD.**—Native plumbic carbonate, $PbCO_3$ (*density* 6·46), is a beautiful mineral found crystallized in transparent needles, or in fibrous masses which are generally opaque. It is soft and brittle, and usually accompanies the deposits of galena, in small quantity. The manufacture of plumbic carbonate, or *white lead*, for the painter is carried on upon a large scale. Several methods are in use in the preparation of this compound; in all of them, however, certain peculiarities in the properties of the acetates of lead are taken advantage of. There are two plumbic acetates—a normal salt, $Pb_2C_2H_3O_2$, and a basic acetate, $Pb_2C_2H_3O_2.2PbO$. A solution of the normal acetate in the presence of an excess of plumbic oxide readily unites with it to form the basic salt, and this basic acetate, if exposed to an atmosphere containing carbonic anhydride, rapidly absorbs this gas, and is thus converted into plumbic carbonate and normal acetate. These changes may be thus represented:

$$\underset{\text{Plumbic acetate.}}{Pb_2C_2H_3O_2} + 2PbO = \underset{\text{Basic plumbic acetate.}}{Pb_2C_2H_3O_2.2PbO}\text{; and}$$

$$\underset{\text{Basic plumbic acetate.}}{Pb_2C_2H_3O_2.2PbO} + 2CO_2 = \underset{\text{Plumbic acetate.}}{Pb_2C_2H_3O_2} + \underset{\text{Plumbic carbonate.}}{2PbCO_3}.$$

The following is the plan which is known as the Dutch method of making white lead: it is still carried on extensively at Lille:—A number of small glazed earthen pots are partially filled with a weak malt vinegar, and in each pot a thin sheet of cast lead coiled into a spiral form or a series of gratings of cast lead is placed; these pots are then embedded in spent tan, arranged in rows, and covered with boards; thus prepared, they are placed in tiers one above another to a depth of 18 or 20 feet,—the warmth given out during the putrefaction of the tan volatilizes the vinegar, and under the united influence of the air and acid fumes, plumbic oxide is formed upon the surface of the coils of

metal; this oxide reacts upon the acetic acid which rises in vapour from the vinegar, and a basic plumbic acetate is thus produced. The carbonic anhydride which is supplied from the decomposing hot-bed readily converts this salt into plumbic carbonate and the normal acetate; whilst the latter again combines with a fresh portion of newly formed oxide, and produces the basic acetate, which is decomposed as before: successive decompositions and recompositions ensue, as the normal acetate immediately combines with any plumbic oxide presented to it, forming the basic acetate, which again is decomposed under the influence of carbonic anhydride. Rolled lead cannot be advantageously substituted for cast lead in this process, and the purest lead is always preferred, traces of iron being sufficient to impart an objectionable yellow tinge to the product.

Since the lead in this process derives oxygen from the air, it is necessary that the atmosphere be allowed to come sufficiently into contact with the coils or gratings. The quantity of vinegar which is required is very small, 1 part of pure acetic acid to 100 parts of lead being amply sufficient. The carbonate is thus produced very slowly, and forms a compact layer upon the surface of the coils. It always contains an excess of hydrated plumbic oxide, but the proportion of this oxide is liable to vary. A specimen which Mulder examined was found to contain $PbH_2O_2.3PbCO_3$; but more usually it consists of $PbH_2O_2.2PbCO_3$. On unrolling the coils, the carbonate breaks off in flakes of a dead-white colour, furnishing the kind of white lead most approved by artists and colourmen. Before it is fitted for their use, it is subjected to the processes of grinding and levigation, by which it is reduced to an impalpable powder. Although this pulverization is performed under water, the fine particles of the carbonate become diffused through the air, rendering the operation very deleterious to the workmen.

This circumstance, combined with the length of time requisite for the formation of the carbonate, induced Thénard to substitute for the foregoing process the direct decomposition of a solution of the basic plumbic acetate, by means of a current of carbonic anhydride; the carbonate is thus procured in a state of extreme division, and as rapidly as can be desired: it has, however, less opacity, or body, owing to its being deposited in exceedingly minute crystals, and is inferior as a pigment to that procured by the Dutch method.

A third process, at one time employed at Birmingham, consisted in exposing litharge, moistened with a solution of normal

plumbic acetate, to a current of impure carbonic anhydride, obtained from the combustion of coke.

Plumbic carbonate is easily decomposed by heat, giving off carbonic anhydride, and leaving a residue of plumbic oxide. It is insoluble in water, unless the water be charged with carbonic acid to a large extent, when it is slightly soluble. It is also soluble in most of the acids with effervescence, and is likewise dissolved by a solution of potassic or sodic hydrate. It is quickly blackened by exposure to sulphuretted hydrogen whether in the gaseous form or in solution in water. This liability to blacken by the action of the gas is possessed by all the salts of lead in common with the carbonate, and is a serious objection to the use of lead compounds as pigments.

White lead is often fraudulently mixed with a considerable quantity of baric sulphate, which is much cheaper, although its whiteness is less intense; a small quantity of indigo, charcoal or plumbic sulphide, is usually added to white lead, in order to substitute a bluish tint for the natural tendency of the white towards yellow.

(1082) **Characters of the Salts of Lead.**—The salts of lead with colourless acids are colourless. The soluble salts even when neutral in composition, redden litmus; but its basic salts have an alkaline reaction. They have a sweetish metallic taste, and exert a poisonous action on the system. In cases of poisoning by a dose of the soluble salts of lead, the best antidote is magnesic or sodic sulphate, which, by double decomposition, forms the insoluble and inert plumbic sulphate. This, however, is of no avail in the more usual forms of lead poisoning, in which the metal is introduced in minute quantities, unintentionally, in water, or in articles of diet.

The best tests for lead are the formation of a white insoluble sulphate when *sulphuric acid* or any of the soluble *sulphates* are added to its solutions; this precipitate is insoluble in potassic cyanide and in acetic acid, but slightly soluble in nitric acid, more readily soluble in excess of potassic hydrate, freely soluble in ammonic acetate; a black sulphide with *sulphuretted hydrogen* and with *ammonic hydric sulphide*, insoluble in excess of the precipitant and in solutions of the alkalies; a yellow chromate with *potassic chromate*, soluble in potassic hydrate; and a yellow iodide with *potassic iodide*. *Hydrochloric acid* and the soluble chlorides give in moderately diluted solutions of lead, a white crystalline precipitate of plumbic chloride, readily soluble in excess of potash. *Potassic hydrate* gives a white precipitate of the hydrated oxide,

which is redissolved in an excess of the fixed alkalies, but is nearly insoluble in ammonia. *Potassic* or *sodic carbonate* gives a dense white precipitate of white lead, which is insoluble in excess of the precipitant. Many other insoluble white salts may be formed, as the phosphate, arsenate, the ferrocyanide, and the cyanide: the latter is insoluble in excess of potassic cyanide, but soluble in dilute nitric acid. All the insoluble salts of lead are soluble in a solution of potassic hydrate. Lead has a remarkable tendency to form basic salts, but the number of its double salts is not great. From the insolubility of many of its organic compounds, it has been much used to determine the combining proportion of organic bodies. It is, however, more advantageous to employ silver for this purpose, because plumbic oxide is slightly volatile.

Lead, like most other metals possessed of comparatively weak attraction for oxygen, is easily precipitated from its solutions in the metallic state, by the metals more oxidizable than itself: if, for instance, a piece of zinc be suspended in a solution containing a compound of lead, such as plumbic acetate, crystals of lead are deposited in a beautiful arborescent form.

Before the blowpipe, on charcoal, the salts of lead yield a soft white malleable bead of the metal, surrounded by a yellow ring of oxide.

(1083) **Estimation of Lead.**—Lead is generally estimated in the form of the sulphate, which contains 68·32 per cent. of the metal. More rarely it is determined from the protoxide, of which 100 parts correspond to 92·83 of lead: porcelain crucibles must be employed for these experiments, since plumbic oxide is easily reduced to the metallic state, in which case it would form an alloy with platinum, and would ruin a crucible composed of this metal.

Lead may be separated by means of sulphuric acid from all the metals, except its insoluble combinations with the metallic acids. The following is the method to be adopted:—If a galena or an alloy of lead is to be analysed, it should be treated with concentrated nitric acid until it is completely decomposed, and then evaporated nearly to dryness with a slight excess of sulphuric acid; the nitric acid is thus expelled, and the metals are converted into sulphates; the mass is treated with water, which dissolves out all the metals except lead, tin, and antimony: quartz and insoluble silicates, as well as baric sulphate, if present, would also be contained in this insoluble portion. The insoluble residue is collected and weighed, and then digested repeatedly in a solution of

ammonic acetate of density 1·065; after which the residue is again washed, dried, and weighed: the difference indicates the proportion of plumbic sulphate, which is dissolved out from the oxides of antimony and tin, and from the quartz and baric sulphate. The lead may be obtained from its solution in the ammonic acetate by the addition of ammonic hydric sulphide; and the plumbic sulphide thus precipitated may be converted into sulphate by means of a mixture of nitric and sulphuric acids. It is evaporated down to dryness, dried, ignited, and weighed.

The salts of lead with the metallic acids may be decomposed by fusing them with a mixture of potassic hydrate and carbonate: the metallic acid forms a salt with potassium, and may be dissolved by the addition of water, whilst a portion of plumbic oxide is left.

§ III. THALLIUM: Tl = 203·6.

(1084) **THALLIUM**: *Density*, 11·81 to 11·91; *Fusing-pt.* 294° (561°·2 F.); *usually Monad, as in* TlCl; *sometimes Triad, as in* $TlCl_3$.—This metal was discovered by Crookes in 1861 (*Phil. Mag.*, [4], xxi. p. 301), as he was examining the spectrum reactions of a seleniferous deposit from the sulphuric acid manufactory of Tilkerode in the Hartz; and in the following year it was obtained more abundantly from a similar source in Belgium by Lamy, to whose paper (*Ann. Chim. Phys.*, 1863, [3], lxvii. 385), and to those of Crookes (*Phil. Trans.*, 1863, and *Jour. Chem. Soc.*, 1864, xvii. 112), the reader is referred for details.

The first indication of its presence was furnished by the occurrence of a single brilliant green line nearly coincident with one of the inconspicuous lines of the barium spectrum, Ba δ (Part I., p. 196, fig. 83, Tl *a*). This green colour suggested to Crookes the name of *thallium* (from θαλλὸς, a budding twig). In the secondary current of an induction-coil, additional lines make their appearance (*Proc. Roy. Soc.*, 1863, xii. 407).

Thallium occurs but sparingly, and has hitherto been principally obtained from the Spanish, Belgium, and Bolivian pyrites. Its compounds have been met with by Bunsen in the mother-liquor of a spring from the Hartz, as well as in some other mineral waters, and particularly in that of Nauheim, in the mother-liquor of which Böttger found it associated with chlorides of cæsium and rubidium. It has also been found by Schrötter in a mica from Zinnwald and in certain samples of lepidolite, and by Hammerbacher in the carnallite of the Stassfurth mines.

Pure thallium is a heavy diamagnetic metal, having a lustre resembling that of cadmium, but tarnishing quickly on exposure to the air. The specific heat of thallium is 0·03355, Regnault (or 0·0325, Lamy), hence the metal, as its compounds show, is of the same class with silver, which it resembles in some of its reactions: like silver and the metals of the alkalies, it may be regarded as a monad. Its atomic volume is 17·16. It is a very crystalline metal, and crackles almost as much as tin when a bar of it is bent; nevertheless it is exceedingly soft, and can readily be scratched with the finger-nail or even by a piece of lead; it may be hammered into foil, and pressed into wire, although its tenacity is small. If rubbed upon paper it leaves a bluish trace resembling that produced by lead, but the streak soon oxidizes and becomes yellowish. It melts at 293°·9 (561° F.; Crookes,) 290° (554° F.) Lamy; oxidizes rapidly in the air, and if heated to about 315° (599° F.), in oxygen, it takes fire, and burns brilliantly with a pure green light. The metal begins to volatilize in the air at a red heat, and below a white heat it boils; it may be distilled in a current of hydrogen. If heated with chlorine, it burns vigorously in the gas, and it also combines directly with bromine, iodine, sulphur, and phosphorus. Nitric acid attacks thallium with great energy; dilute sulphuric acid also dissolves it quickly with evolution of hydrogen, but the action of hydrochloric acid, even when boiled with it, is but slow, owing to the insolubility of the chloride. The tarnished metal becomes bright when plunged into water, owing to the solubility of the oxide; but the metal may be preserved in water unaltered. Thallium may be easily alloyed with most of the metals, particularly zinc, lead, antimony, tin, copper, silver, and platinum.

The best source of the metal is the thalliferous dust deposited in the flues of the sulphuric acid works where thalliferous pyrites are employed. This is boiled with dilute sulphuric acid, filtered, and the clear liquors are mixed with a large excess of strong hydrochloric acid, which precipitates impure thallious chloride.* This is washed, and then converted into thallic peroxide by suspending it in a solution of sodic carbonate and passing chlorine into the liquid. The product after being well washed is suspended in water, and transformed into pure thallious sulphate by a current

* As, however, the whole of the thallium is not precipitated by this means, Nietzki recommends (*Arch. Pharm.*, [2], vii. 385) to precipitate the filtrate from the chloride with potassic iodide, which throws down the whole of the thallium as iodide: this may be converted into the sulphide by treatment with sodic sulphide, and the sulphide into sulphate by dilute sulphuric acid.

of sulphurous anhydride. The solution on evaporation yields the sulphate in a crystalline state. It may be recrystallized, and if the solution be decomposed by metallic zinc, or by the voltaic battery, pure thallium is abundantly and easily obtained. The chloride can also be converted into the sulphate by treatment with a very dilute solution of sodic sulphate in the cold, and the thallium precipitated from the solution by pure zinc after being slightly acidulated with sulphuric acid. The metal can be melted in an iron crucible heated by a gas flame, maintaining a current of coal-gas through the crucible to prevent oxidation, or else under potassic cyanide.

Metallic thallium may also be obtained directly from the chloride by fusing it with sodic carbonate and lamp-black, but there is always a slight loss.

(1085) **THALLIOUS CHLORIDE**, TlCl, is a yellowish-white, sparingly soluble compound, less soluble in hydrochloric acid than in water, sparingly soluble in ammonia; it forms a red crystalline double salt with ferric chloride, having the composition, $6TlCl.Fe_2Cl_6$, which is soluble in hot concentrated hydrochloric acid, but is immediately decomposed by water; it also forms double salts with the chlorides of gold and platinum. Lamy has described three other chlorides, Tl_2Cl_3 and $TlCl_2$, and one with still more chlorine, $TlCl_3$. The chloride, Tl_2Cl_3, is obtained in yellow scales on heating thallious chloride in a current of chlorine. Several bromides and iodides of thallium exist: the *protiodide* and *bromide* are yellow and sparingly soluble. Thallious iodide when heated undergoes a change similar to mercuric iodide, but of an opposite character; the yellow compound becoming scarlet when heated.

(1086) **OXIDES OF THALLIUM.**—Thallium appears to form three oxides—a suboxide of unknown composition; an oxide corresponding to the principal oxide of silver, Tl_2O; and a superior brown oxide, thallic oxide, Tl_2O_3, formed at the positive electrode during electrolysis of thallious sulphate by a weak current, or by the action of hydric peroxide on metallic thallium, or by warming freshly precipitated thallious chloride with a solution of sodium hypochlorite, or, what amounts to the same thing, by passing a current of chlorine into sodic carbonate containing the chloride in suspension. When dried over sulphuric acid it has the composition, $Tl_2O_3.OH_2$ or $Tl'''HO_2$.

The most important of these is *thallious oxide*, Tl_2O; this is very soluble in water, furnishing an alkaline caustic solution which absorbs carbonic anhydride from the air. The solution is

colourless, and by evaporation *in vacuo* yields groups of pale-yellow, prismatic needles of the hydrate, TlHO, which blacken as the evaporation proceeds; when heated at about 315° (599° F.) it becomes anhydrous, and fuses to a brown liquid, which becomes yellow on cooling. A solution of thallious oxide causes a precipitate in solutions of salts of magnesium, manganese, zinc, lead, iron, and many other metals, but does not redissolve the precipitate, even if the thallious oxide be in excess.

(1087) **DITHALLIOUS SULPHIDE**, or *Sulphide of thallium*, Tl_2S, may be obtained as a black, shining, brittle mass by fusing, at the heat of a blast furnace, sulphur and thallium in the proportion of one atom of the former to two of the latter, or as a brownish-black curdy precipitate, by adding ammonic hydric sulphide to the soluble thallious salts. The precipitate is not soluble in excess of the alkaline sulphides. Thallious acetate and oxalate in neutral solutions are precipitated by sulphuretted hydrogen. A thallic sulphide, Tl_2S_3, has also been obtained, and Schneider states that a compound, Tl_6S_7, is formed on fusing a mixture of thallious sulphate, sodic carbonate, and sulphur.

(1088) **THALLIOUS SULPHATE**, or *Sulphate of thallium*, Tl_2SO_4, is a soluble salt crystallizing in anhydrous six-sided prisms which are easily fusible. With aluminic sulphate it furnishes an octahedral alum, a property which may be taken advantage of in the preparation of thallium from flue dust (*Chem. Centr.*, 1874, 118). An acid thallious sulphate exists.

(1089) **THALLIOUS NITRATE**, $TlNO_3$, crystallizes in anhydrous, prismatic needles which melt easily: they are isomorphous with potassic nitrate, and are insoluble in alcohol. It is readily obtained by dissolving the metal in nitric acid.

(1090) **THALLIOUS CARBONATE**, Tl_2CO_3, furnishes long, flattened, prismatic needles, which require about 25 parts of cold water for solution. It is easily fusible.

The *phosphate* is sparingly soluble, and is fusible.

(1091) **Characters of the Salts of Thallium.**—The *thallious salts* are poisonous when taken internally. They are nearly colourless, when formed with colourless acids; solutions of the salts of thallium are easily decomposed by a feeble electric current, with deposition of plates of the metal upon the negative electrode. *Metallic zinc* also precipitates finely-divided metallic thallium, but tin does not reduce the metal.

No precipitate is produced in solutions of the thallious sulphate or nitrate by the *hydrated alkalies*; the *carbonates* give a precipitate only in concentrated solutions. *Sulphuretted hydrogen*

gives but little precipitate in solutions of thallious nitrate, chloride, or sulphate. *Ammonic hydric sulphide* gives a brownish-black precipitate insoluble in the sulphides of the alkali-metals. *Chlorides* and *bromides* give yellowish-white, sparingly soluble precipitates; the *iodides* give a reddish-yellow precipitate; *potassic cyanide*, a white precipitate soluble in excess of the precipitant; *potassic chromate*, a pale yellow precipitate soluble in dilute acids, insoluble in ammonia. With *platinic chloride* it forms a sparingly soluble double salt, $TlCl.PtCl_4$.

§ IV. INDIUM: In=113·4.

(1092) **INDIUM**; *Density*, 7·42; *Fusing-pt.* 176° (349° F.); *Triad as in* $InCl_3$.—This rare metal was discovered by Reich and Richter in the zinc-blende of Freiberg, in 1863, by means of its peculiar and characteristic spectrum, consisting of two bright lines in the blue and indigo, not coincident with those of any other known body. One of these lines is rather more refrangible than the blue line of strontium, the other feebler line is near the violet line of potassium, but is less refrangible than it. This suggested the name of *indium* for the new body. It usually occurs associated with zinc, and is most conveniently obtained from Freiberg zinc by the process suggested by Bayer. The metal is treated with a quantity of hydrochloric acid insufficient to completely dissolve it, and the undissolved portion is allowed to remain in the liquid for two or three days, by which means all the indium is precipitated on the zinc. The clear solution of zincic chloride is decanted, and the metallic mud, after the removal of the unattacked zinc, is treated with a few drops of dilute sulphuric acid to dissolve any zincic oxychloride that may have been formed; it is then thoroughly washed with hot water. The product is heated with nitric acid, sulphuric acid is added, and the whole evaporated to dryness in order to separate the tin and lead in the form of oxide and sulphate. The residue is now extracted by boiling water and an excess of ammonia added to the filtered solution, thereby precipitating the indium and iron, and leaving the copper, zinc, and cadmium in solution. This precipitate, after being well washed, is dissolved in the smallest possible quantity of hydrochloric acid, mixed with sodic hydric sulphite in excess, and boiled until the odour of sulphurous anhydride has disappeared. The whole of the indium is thus obtained as sulphite, perfectly free from zinc, cadmium, copper, and iron. In order to remove any lead that may be pre-

sent, the crystalline precipitate is dissolved in sulphurous acid, filtered, and again precipitated by boiling; it is then quite pure, and has the formula, $2In_2O_3.3SO_2.8OH_2$. By treating it with dilute acids the other salts of indium can readily be prepared.

Metallic indium may be obtained from its oxide by heating it with sodium or in a current of hydrogen. Böttger prefers to precipitate the metal from its solution by pure zinc, and after washing and pressing the spongy mass, to fuse it into a button under potassic cyanide. It is a white metal much resembling lead in appearance, soft, ductile, and destitute of crystalline structure. Its density is 7·421 at 16°·8 (62°·3 F.), and according to Bunsen its specific heat is ·0569. It melts at 176° (349° F.), but is much less volatile than cadmium or zinc. It does not oxidize readily at a low temperature, but at a bright red heat it burns with a violet flame, forming the yellow oxide. It dissolves slowly in dilute sulphuric or hydrochloric acid with evolution of hydrogen, rapidly in strong hydrochloric acid. Nitric acid oxidizes it with evolution of nitrous fumes.

(1093) **INDIC CHLORIDE**; In_2Cl_6.—When indium is strongly heated in an atmosphere of chlorine it burns with a greenish light, producing the chloride, which sublimes at a very high temperature in white laminæ. It may also be obtained by dissolving the metal or its sulphite in hydrochloric acid. It forms crystalline double salts with the alkali-metals.

Indic Bromide, In_2Br_6, formed by the direct union of bromine and the metal, is a white crystalline substance which volatilizes readily.

Indic Iodide, In_2I_6, is also crystalline, and deliquesces when exposed to the air.

(1094) **OXIDES OF INDIUM.**—There are several indium oxides, of which the yellow oxide, In_2O_3, obtained by igniting the hydrate, is the best defined. It is not volatile even at a white heat, and is readily soluble in acids. On adding ammonia to a boiling solution of an indic salt, the hydrate is precipitated; dried at 100° (212° F.), it has the composition represented by $In_2H_6O_6$. On heating indic oxide to various temperatures in a stream of hydrogen, three other oxides are obtained: at 180° (356° F.) a green substance to which the formula In_7O_9 has been assigned; at 220° (428° F.) a grey oxide, In_4O_5; and at 300° (572° F.) a black compound, perhaps InO. It has not, however, as yet been satisfactorily established that these substances are definite compounds.

(1095) **INDIC SULPHIDE,** In_2S_3, is obtained in glistening scales on fusing metallic indium or indic oxide with sulphur. Sulphuretted hydrogen produces a deep yellow-coloured precipitate of the sulphide in an acetic acid solution; this becomes brown when dry, and is decomposed by mineral acids. A double salt of this sulphide with potassic sulphide, of the formula $K_2S.In_2S_3$, has been obtained. It crystallizes in red, lustrous, quadratic tables.

(1096) **Indic Sulphate** is obtained as a gummy mass on evaporating its solution at 100° (212° F.); when strongly heated it leaves a basic salt. A crystalline *indic ammonic alum,* $In_2(NH_4)_23SO_4$, has been obtained.

Indic nitrate, $In_26NO_3.9OH_2$, crystallizes in long prisms or needles which lose $6OH_2$ at 100° (212° F.).

Indic carbonate is a white gelatinous precipitate, formed on adding a carbonate to an indic salt; it is soluble in ammonic carbonate, but is reprecipitated on boiling.

(1097) **Characters of the Salts of Indium.**—Indium is precipitated from its solution, in the metallic state, by cadmium and zinc, and as sulphide by *sulphuretted hydrogen,* provided the solution is not strongly acidulated with a mineral acid. *Alkaline carbonates* produce a white precipitate insoluble in excess. *Potassic* and *sodic hydrates, ammonic carbonate,* and *potassic cyanide,* white precipitates soluble in excess. *Potassic chromate* yields a yellow precipitate, and *potassic ferrocyanide* a white one. Indium is completely precipitated from its solutions as sulphite on boiling them with excess of hydric sodic sulphite; advantage may be taken of this in the quantitative estimation of the metal.

CHAPTER XXIV.

GROUP VIII.

THE NOBLE METALS.

(1098) In the group of metals with which we conclude, there is a less intimate natural relationship than in any of the preceding ones. We have, for instance, in silver a monad element, in mercury a dyad, in gold a triad, and in platinum a

tetrad element; whilst the relations of the remaining metals have been but incompletely ascertained.

It is, notwithstanding, convenient for the present to group them together. The following table shows in one view, some of the most important numerical constants of the metals enumerated in this division which have as yet been determined:

Metals.	Symbol.	Atomic weight.	Atomic vol.	Specific heat.	Fusing point. °C.	Fusing point. °F.	Density.	Electric conductivity at 0° C.
Mercury ...	Hg	200·0	14·72	0·0319	−38·8	−37·9	13·59	1·63*
Silver ...	Ag	108·0	10·26	0·0570	916	1681	10·53	100·00
Gold	Au	196·6	10·17	0·0324	1037	1899	19·34	77·96
Platinum ...	Pt	197·1	9·15	0·0324	1460	2660	21·53	10·53†
Palladium ...	Pd	106·5	9·02	0·0593	1360	2480	11·8	12·64‡
Rhodium ...	Ro	104·3	8·62	0·0580			12·1	
Ruthenium ...	Ru	104·2	9·14				11·4	
Osmium ...	Os	199·0	9·30	0·0306			21·4	
Iridium ...	Ir	198·0	9·36	0·0326			21·15	
Davyum ...		154·0					9·39	

§ I. MERCURY: Hg=200.

(1099) **MERCURY**: *Density as Liquid at* 0° (32° F.), 13·596; *as Vapour, Theoretic,* 6·92; *Observed,* 6·976; *Pseudo-monad in Mercurous salts, as* Hg_2Cl_2; *Dyad in Mercuric salts, as* $HgCl_2$; *Rel. wt.* 100; *Melting-pt.* −38°·8 (−37°·9 F.); *Boiling-pt.* 357° (674·6° F.); *Atomic and Mol. Vol.* [ ].§—Mercury (*hydrargyrum*, from ὕδωρ, ἄργυρον, 'liquid silver,' or *Quicksilver*) is one of the metals which have been longest known; it is found in but few localities, and occurs most frequently in the form of the sulphide (cinnabar), usually accompanied by small quantities of the metal in its native state. Occasionally it is met with as an amalgam combined with silver, sometimes as chloride in the form of calomel, and more rarely in that of iodide. Generally speaking, its ores are found in clay-slate, or in the red sandstone underlying the coal, and not unfrequently among the coal-measures themselves. The most productive mines are those of Almaden, in Spain: very extensive and valuble deposits of cinnabar have likewise lately been found in California, and the mines of Idria, in Transylvania, have long been extensively worked. Consider-

* At 22°·8 C. † At 20°·7 ‡ At 17°·2.

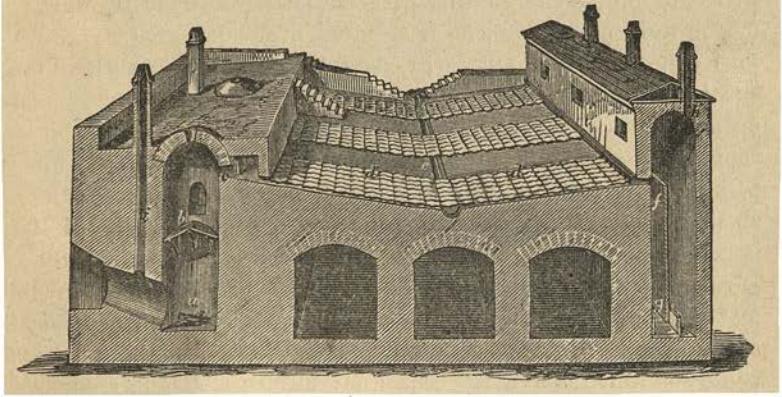
§ The molecule of the vapour of mercury contains only 1 atom of the metal Hg. like zinc, cadmium, and other metallic dyads.

able quantities are likewise raised in China, Japan, and Borneo, and from the mine of Huancavelica, in Peru.

Extraction.—The metal may be obtained from its ore either by burning off the sulphur and distilling the mercury,—a process which is applicable both to cinnabar and to the native metal,—or by heating the cinnabar with some substance capable of forming a fixed compound with the sulphur, when the liberated mercury distils off.

At Almaden, the metal is extracted by the first process. The ore employed yields about 10 per cent. of mercury. Fig. 364 shows a section of the furnace

FIG. 364.



made use of:—Each furnace contains two grates; and on the lower one, *a*, provided with a chimney, *i*, a fire of brushwood is kindled; the upper grating is formed by a brick arch, *b*, perforated with numerous apertures; on this arch the sulphide rests, the poorer pieces of ore being placed at the bottom. The brushwood quickly kindles the sulphur in the ore, which afterwards by its combustion maintains sufficient heat to continue the operation without the use of any other fuel; sulphurous anhydride is formed, and the liberated mercury distils, and is condensed in wide earthen pipes, *d*, *d*, connected with the upper aperture, *c*, of the furnaces; these pipes are termed *aludels*. The aludels are supported on a doubly inclined plane of masonry; at the lowest point a perforation is made, to allow of the escape of the mercury into a brick channel, *e*, through which it runs into a well; the further end, *f*, of the aludels opens into a condensing chamber, in which an additional quantity of mercury is deposited in the trough, *g*: the sulphurous anhydride escapes into the air through the chimney, *h*. Considerable waste of metal is incurred during this process, from the incomplete manner in which the condensation is effected. Iron pipes, however, cannot be substituted for the earthen ones, as they become corroded rapidly by the acid vapours produced in the operation.

At Idria the process of the extraction is the same in principle as at Almaden, but the condensation is effected more completely by transmitting the mercurial vapours through a succession of chambers of masonry, instead of through aludels.

Another plan which is practised in the Palatinate consists in mixing the sulphide with slaked lime, and conducting the distil-

lation in cast-iron furnaces and retorts. The mercury is condensed in receivers partly filled with water, whilst calcic sulphide and sulphate remain behind in the retort: $4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$. Iron filings also decompose cinnabar when heated with it, ferrous sulphide being formed whilst mercury is liberated. Experience has shown that unless the ore contains at least $\frac{1}{600}$ of its weight of the metal, or 3·8 lb. per ton, it is too poor to be advantageously worked by the methods at present in use.

Purification.—If the ore contains any admixture of zinc and bismuth, small portions of these metals are liable to distil over with the mercury. In this case a film forms upon the surface of the fluid metal when it is agitated in contact with air. The purity of the product is easily seen by the absence of this film, and by the perfect mobility and sphericity of the globules, which do not wet the surface of non-metallic objects. Violette finds that the distillation of mercury on the large scale is much facilitated by transmitting a current of superheated steam at about 371° (700° F.), through the retort in which the distillation is being effected. A small quantity of mercury may be rapidly purified by placing it in a bottle, with a little finely-powdered loaf-sugar; the mercury should not occupy more than one-fourth of the capacity of the bottle: the bottle is then closed, and briskly agitated for a few minutes; after which the stopper is withdrawn, and fresh air is blown into the bottle with a pair of bellows, and the agitation is repeated; this is done three or four times, and the mercury is then poured into a cone of smooth writing-paper in the apex of which a pin-hole is made; the metal runs through, and leaves the powdered sugar mixed with the oxides of the foreign metals, and a considerable quantity of finely-divided mercury.

Generally speaking, the mercury imported into this country is almost chemically pure. Any foreign metals which may be present in it may be removed by allowing it to stand for some days covered with a stratum of dilute nitric acid; the mercury should be placed in a shallow dish, so as to expose a large surface to the acid, and it should be frequently agitated; the acid exerts but little action on the mercury so long as any more oxidizable metals are present. A solution of mercuric nitrate may be substituted for the nitric acid with advantage; in this case the mercury is deposited from the solution and takes the place of the other metals, which are dissolved. A convenient method of keeping mercury in a pure and dry state in the laboratory has

been suggested by Deville; the metal is placed in a large glass vessel with a stopcock at the bottom, and is covered with a layer of concentrated sulphuric acid saturated with mercurous sulphate, which gradually removes all the more electropositive metals with precipitation of metallic mercury. When required for use, the mercury is drawn off at the bottom of the vessel and should be returned to it when done with.

(1100) **Properties of Mercury.**—Mercury, which possesses a lustre resembling that of polished silver, is the only metal that is fluid at common temperatures, with the exception, possibly, of cæsium. It freezes at $-38°{\cdot}8$ ($-37°{\cdot}9$ F.), and contracts considerably at the moment of congelation, crystallizing in octahedra: in this state it is malleable: its density at its fusing point referred to water at 4° (39°·2 F.) is 14·1932 (Mallet). It boils at 357°·25 (675° F.), under a pressure of $760^{mm.}$ (Regnault), and forms an invisible, transparent vapour, of density 6·976. The metal, even at a temperature of $-41°$ ($-41°{\cdot}8$ F.) volatilizes. Its density at 4° (39°·2 F.), reduced to a vacuum and compared with water at the same temperature is 13·594 (Balfour Stewart), and at 15°·5 (60° F.) is 13·56. When pure, it is not tarnished by exposure to air and moisture at ordinary temperatures, but if heated at about 371° (700° F.) or 426° (800° F.) it absorbs oxygen, and is gradually converted into the red oxide. Mercury enters into combination with chlorine, bromine, and with many of the metals at the ordinary temperature. It also unites both with sulphur and with iodine without the aid of heat, if triturated with them. Hydrochloric acid whether cold or hot is without action upon the metal. Hydriodic acid and sulphuretted hydrogen are slowly decomposed by it, with evolution of hydrogen. Concentrated sulphuric acid produces no change in the cold, but is decomposed when heated with it, sulphurous anhydride being evolved, whilst the mercury is converted into sulphate. Strong nitric acid dissolves it with rapidity, forming mercuric nitrate, whilst nitric oxide is evolved in abundance. If the acid be dilute, and the metal in excess, the mercury is slowly dissolved, and at ordinary temperatures, mercurous nitrate is the result. Mercury may be obtained in a very finely divided state, by precipitating a solution of mercuric chloride with a solution of stannous chloride: the stannous salt, if added in sufficient quantity, removes all the chlorine, and the mercury subsides as a grey metallic powder; $HgCl_2 + SnCl_2 = Hg + SnCl_4$.

(1101) **Uses of Mercury.**—Mercury is extensively employed in the extraction of gold and silver from their ores by the process of amalgamation, large quantities being annually sent to South America for this purpose. Its amalgams are largely employed in the processes of silvering and gilding. Mercury also combines readily with lead, copper, bismuth, tin, zinc, magnesium, potassium, and sodium, forming amalgams which are easily dissolved by an excess of mercury. Joule succeeded in many cases in obtaining definite compounds of various metals with mercury, by subjecting their semi-solid amalgams to powerful hydraulic pressure, amounting to 60 tons upon the square inch: with platinum 1 atom was united with 2 atoms of mercury. With silver, copper, and iron, the amalgams contained 1 atom of each metal; with zinc and lead, the amalgam in each case contained 1 atom of mercury with 2 atoms of the other metals, whilst the amalgam of tin was represented by the formula, Sn_7Hg. Sodium amalgam is a most valuable reducing agent, especially in organic chemistry; it is most conveniently prepared by adding the sodium in small portions at a time to mercury heated under a layer of melted paraffin. According to E. de Souza, sodium amalgam containing excess of mercury leaves the compound, Na_3Hg, when heated at 440° (824° F.), whilst potassium gives the compound, K_2Hg.

Mercury is indispensable in the construction of philosophical instruments, and is also used in the preparation of vermilion, which is highly valued as a pigment, for the purity and permanence of its tint. It is well known in various forms as a valuable medicine; it exerts a powerful action upon the animal economy, producing salivation, and seriously impairing the health of the workmen exposed to its vapours, giving rise to a remarkable tremulous state, known as *mercurial palsy*, consequent upon a peculiar form of nervous debility. By trituration with saccharine or oleaginous substances, it admits of being minutely subdivided, and a small portion of it becomes oxidized, to which the active properties of blue-pill appear to be owing; the same remark applies to the mercurial ointment, and the *pulvis hydrargyri cum cretâ*.

(1102) **MERCUROUS CHLORIDE**, or *Calomel*; $Hg_2Cl_2=471$; *Density of Vapour, Theoretic,* 8·148; *Observed,* 8·35; *of Solid,* 7·14; *Mol. Vol. anomalous,* [ ]*; *Rel. wt.* 117·75; *Comp. in*

* The anomalous vapour density of mercurous chloride is most probably due to its dissociation into 2 vols. of mercuric chloride, and two of mercury vapour.

100 *parts*, Hg, 84·92; Cl, 15·08.—Mercury forms two compounds with chlorine, one of which, mercuric chloride, $HgCl_2$, is known as corrosive sublimate, whilst the other, Hg_2Cl_2, is calomel. The latter may be obtained by precipitating a solution of mercurous nitrate by one of common salt, but it is generally prepared by sublimation; 13 parts of mercury are triturated with 17 of corrosive sublimate, until no metallic globules are visible, the dichloride having been previously moistened with water or alcohol, to prevent the acrid particles from being diffused through the air, the mixture is then sublimed in suitable vessels, and the calomel is deposited as a semi-transparent, fibrous cake. In this operation the additional mercury combines with half the chlorine of the dichloride: $HgCl_2 + Hg = Hg_2Cl_2$. Sometimes the vapours are sent into a capacious chamber; the deposit then assumes the form of a fine powder. The salt may also be obtained by the decomposition of mercurous sulphate with sodic chloride. For this purpose 1 kilo. of mercury may be converted into sulphate by boiling it to dryness with 1·5 kilo. of sulphuric acid; the residue is then to be intimately mixed with 1 kilo. more of mercury, and subsequently triturated with 0·75 kilo. of sodic chloride, after which it is to be sublimed. The mercuric sulphate which is first obtained is converted into mercurous sulphate by the addition of the second portion of mercury, and this in its turn is decomposed into calomel and sodic sulphate when heated with sodic chloride: $Hg''SO_4 + Hg = (Hg_2)''SO_4$; and $(Hg_2)''SO_4 + 2NaCl = Na_2SO_4 + Hg_2Cl_2$. Calomel may also be prepared by forming a saturated solution of corrosive sublimate in water at 50° (122° F.), and passing sulphurous anhydride into the hot liquid; calomel is then precipitated in minute crystals, whilst sulphuric and hydrochloric acids are liberated;

$$2HgCl_2 + 2OH_2 + SO_2 = Hg_2Cl_2 + 2HCl + H_2SO_4.$$

The mercurous compounds appear to contain mercury in the pseudo-monad condition, two atoms forming a dyad group $(Hg_2)''$; thus mercurous chloride becomes $(Hg_2)Cl_2$ $\left[\begin{matrix}\mathbf{HgCl}\\ \mathbf{HgCl'}\end{matrix}\right.$ or graphically, Cl—Hg—Hg—Cl].

When prepared by sublimation, calomel requires careful washing and levigation, because portions of the undecomposed dichloride always sublime with the calomel, and they can only be removed by repeated washing. It was formerly supposed that the medicinal character of calomel was rendered milder by repeated sublimations. This, however, has been found to be a serious mistake, for every time that calomel is sublimed, a small

portion of it is reconverted into mercuric chloride and metallic mercury. The presence of $\frac{1}{50,000}$ of the dichloride in calomel may be detected, according to Bonnewyn, by placing the calomel, moistened with alcohol or ether, on a polished knife-blade; a black spot is formed if any corrosive sublimate be present.

Properties.—Calomel sublimes in quadrilateral prisms terminated by four-sided pyramids; when powdered it is of a yellowish-white colour. It begins to sublime below redness, and before undergoing fusion. Calomel is tasteless and insoluble in water; sodic and potassic hydrates decompose it, forming mercurous oxide. Lime-water has a similar effect, and when mixed with a small proportion of calomel it furnishes what is known as *black wash.* Solution of ammonia forms with calomel a black compound, consisting of $NH_2(Hg_2)''Cl$: this change is explained in the subjoined equation; $Hg_2Cl_2 + 2NH_3 = NH_2Hg_2Cl + NH_4Cl$. This black compound may be regarded as ammonic chloride in which the dyad group $(Hg_2)''$ has taken the place of two atoms of hydrogen. Ammoniacal gas is absorbed by precipitated calomel at ordinary temperatures, and a compound containing $N_2H_6(Hg_2)''Cl_2$ is formed, or two molecules of ammonic chloride in which two of the atoms of hydrogen have been displaced by $(Hg_2)''$. Sulphuric acid is without action on calomel; boiling nitric acid dissolves it, and forms mercuric chloride and mercuric nitrate; a solution of chlorine converts it slowly into mercuric chloride; if boiled for a long time with hydrochloric acid or sodic chloride, it is resolved into mercuric chloride and metallic mercury: the same effect is produced, but more rapidly, by boiling it with a solution of ammonic chloride.

(1103) **MERCURIC DICHLORIDE,** or *Bichloride of mercury, Corrosive sublimate;* $HgCl_2 = 271$; *Density, of Vapour,* 9·8; *of Solid,* 5·42; *Mol. Vol.* [ ]; *Rel. wt.* 135·5; *Comp. in* 100 *parts,* Hg, 73·8; Cl, 26·2.—When heated mercury is placed in an atmosphere of chlorine it ignites from the rapid union of the gas with the metal, and the dichloride is formed. It is prepared on the large scale by decomposing basic mercuric sulphate with hydrochloric acid or by mixing intimately 2½ parts of mercuric sulphate with 1 of common salt, and subliming the mixture in glass vessels at a carefully regulated heat; in the latter case sodic sulphate remains in the vessel, and the dichloride sublimes; $HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$. The fumes are extremely acrid and poisonous.

Properties.—Mercuric chloride fuses at 265° (509° F.), and boils at 295° (563° F.); its vapours are condensed in snow-white,

crystalline needles, or in octahedra with a rectangular base. As sold in the shops, it occurs in transparent, colourless masses, which have a crystalline fracture. It has an acrid, burning taste, and disagreeable, metallic flavour. It is soluble in 16 parts of cold water, and in less than 3 of boiling water, the concentrated solution depositing it as it cools in transparent, anhydrous, quadrilateral prisms. Its aqueous solution reddens litmus, and by long exposure to light, is gradually decomposed, calomel being deposited. Alcohol when cold dissolves nearly one-third of its weight of the salt, and its own weight when boiling; ether also dissolves it freely. If an aqueous solution of mercuric chloride be agitated with ether, almost the whole of the salt will be abstracted by it from the water, and the ethereal solution will rise to the surface. It is very soluble in solutions of the alkaline chlorides, with which it enters into combination, forming double salts.

With potassic chloride it forms three distinct crystallizable compounds, $KCl.2HgCl_2.2OH_2$; $KCl.HgCl_2\,OH_2$; and $2KCl.HgCl_2.OH_2$. They are easily prepared by dissolving the salts in the proper proportions, and allowing them to crystallize. With sodic chloride only one such compound is formed, $2(NaCl.HgCl_2).3OH_2$. A salt with ammonic chloride, $2NH_4Cl.HgCl_2.OH_2$, has long been known as *sal alembroth:* it crystallizes in flattened rhomboidal tables.

Similar compounds having a composition analogous to that of the sodium salt may be formed with most of the soluble chlorides. Calcic and magnesic chlorides form more than one compound. An analogous but anhydrous salt, $HCl.HgCl_2$, is formed by dissolving mercuric chloride in hot hydrochloric acid, from which it crystallizes on cooling; it is, however, decomposed by water.

Mercuric chloride combines with the sulphide, forming a white, insoluble, gelatinous compound, consisting of $2HgS.HgCl_2$; it is the white precipitate which is always formed at first, on passing a current of sulphuretted hydrogen through a solution of mercuric chloride.

Mercuric chloride is decomposed by the hydrates of the fixed alkalies and alkaline earths, a chloride of the alkali-metal and mercuric oxide being formed. When ammonia is added to a solution of mercuric chloride, it separates only half the chlorine, uniting with the remainder to form the compound called white precipitate (1104). Mercuric chloride acts powerfully on the albuminous tissues, and combines with them; it is a violent and acrid poison. The best antidote in cases of poisoning with this substance is the immediate administration of the whites of several raw eggs, as it coagulates the albumin, and forms with it a sparingly soluble compound. It was supposed that the dichloride was converted into calomel, but this does not appear to be the case. Owing to this action of the dichloride

upon albumin, corrosive sublimate is a powerful antiseptic; a solution of this salt is hence often employed to preserve anatomical preparations: wood, cordage, and canvas, if soaked in a solution of the salt containing 1 part of it in 60 or 80 parts of water become much less liable to decay when exposed to the combined action of air and moisture.

(1104) **Action of Ammonia on Corrosive Sublimate.**—When a solution of mercuric chloride is added to a solution of ammonia in excess, one-half of the chlorine only is removed from the salt, and the so-called infusible *white precipitate, mercurius precipitatus albus,* is formed; this, after being washed with cold water, is completely soluble in nitric and in hydrochloric acids, and therefore cannot contain any calomel; $HgCl_2 + 2NH_3 = NH_2Hg''Cl + NH_4Cl$. Kane considered this white precipitate as a compound of chloride with amide of mercury, $N_2H_4Hg.HgCl_2$ (p. 490); but it may also be regarded as mercurammonic chloride or ammonic chloride, in which 2 atoms of hydrogen are displaced by the bivalent atom of mercury, $NH_2Hg''Cl$. If ammonia be added drop by drop to a solution of mercuric chloride, which is purposely maintained in considerable excess, the precipitate consists of $N_2H_4Hg_4Cl_6$; this formula would be that of 2 molecules of ammonic chloride, in which 4 atoms of the hydrogen are replaced by an equivalent quantity of the monad group, $(HgCl)'$ or $N_2H_4(HgCl)'_4Cl_2$, or it may be regarded as a compound of mercurammonic chloride with mercuric chloride, $2NH_2Hg''Cl.2HgCl_2$.

White precipitate has been made the subject of numerous experiments. If it be heated at about 320° (608° F.), ammonia and the ammoniated chloride of mercury are expelled, and a red crystalline powder remains having a composition represented by the formula, $N_2Hg_3.2HgCl_2$; for $6NH_2Hg''Cl = 3NH_3 + NH_3.HgCl_2 + N_2Hg_3.2HgCl_2$. This red powder is insoluble in water and in dilute acids, but it is dissolved and decomposed by boiling hydrochloric acid and by sulphuric acid. By raising the temperature still further it is decomposed into nitrogen, metallic mercury, and calomel. It is interesting, as it appears to contain a double molecule of ammonia in which the 6 atoms of hydrogen are displaced by 3 bivalent atoms of mercury.

When white precipitate is boiled in water it is decomposed, and the heavy insoluble canary-yellow mercuramine chloride is formed, whilst ammonic chloride remains in the solution: $4NH_2Hg''Cl + 2OH_2 = N_2Hg_4Cl_2.2OH_2 + 2NH_4Cl$. This yellow powder is easily dissolved by dilute nitric or hydrochloric acid. It may be regarded as a compound of mercurammonic chloride with mercuric oxide, $N_2Hg''_4Cl_2.2OH_2 = 2NH_2Hg''Cl.2HgO$.

Chlorine and bromine both act violently on white precipitate, forming mercuric chloride or bromide, the action in many cases being attended with explosion. With iodine, an explosion almost invariably takes place after a few minutes: it would appear that iodide of nitrogen is formed.

If a solution of mercuric chloride be added gradually to a boiling solution

of ammonic chloride and free ammonia as long as the precipitate is redissolved on agitation, a compound crystallizes in rhombohedra on cooling; and the same substance is formed on boiling ordinary white precipitate in a solution of ammonic chloride. This compound fuses and undergoes decomposition at a temperature of 300° (572° F.); boiling water extracts a large proportion of ammonic chloride from it, and leaves the canary-yellow powder above described. It is freely soluble in acids, even in acetic acid. Kane's analysis of this compound would allow of its being represented by the formula, $N_2H_6Hg''Cl_2$. It is sometimes called *fusible white precipitate.*

When mercuric chloride is exposed to a current of dry ammoniacal gas, it fuses, with development of heat; 1 molecule of the salt absorbs 1 of ammonia, producing $NH_3.HgCl_2$. This compound may be sublimed without change, but it is decomposed by water: it is a true ammoniated mercuric dichloride.

The following table shows the principal compounds produced by the combined action of ammonia and heat upon mercuric chloride:

(1) White precipitate	$NH_2Hg''Cl$ or $N_2H_4Hg''_2Cl_2$.
(2) Red crystalline compound ...	$N_2Hg''_3.2HgCl_2$.
(3) Mercuramine chloride	$N_2Hg_4Cl_2.2OH_2$ or $N_2H_4Hg''_2Cl_2.2HgO$.
(4) Mercuramine perchloride ...	$N_2H_4(HgCl)_4Cl_2$ or $N_2H_4Hg''_2Cl_2.2HgCl_2$.
(5) Fusible white precipitate ...	$N_2H_6Hg''Cl_2$.
(6) Ammoniated mercuric dichloride	$NH_3.HgCl_2$.

besides the double salts, of which one is—

(7) Sal alembroth	$2NH_4Cl.HgCl_2.OH_2$.
(8) And another is	$NH_4Cl.HgCl_2$.

These remarkable compounds derive interest from their connexion with the theories which have been proposed respecting the nature of ammonia, the consideration of which will be resumed when the alkaloïds or organic bases are examined.

(1105) **BROMIDES OF MERCURY.**—Two of these analogous to the chlorides of mercury, may be formed; they yield corresponding double salts; both of them may be sublimed without undergoing decomposition. *Mercurous bromide* ($Hg_2Br_2 = 560$; *density of vapour, theoretic,* 9·688; *observed,* 10·14; *mol. vol. anomalous,* ⊢⊣; *rel. wt.* 140) is white and insoluble. *Mercuric bromide* ($HgBr_2 = 360$; *density of vapour, theoretic,* 12·456; *observed,* 12·16; *mol. vol.* ⊢⊣; *rel. wt.* 180) is crystallizable and soluble.

(1106) **IODIDES OF MERCURY.**—Mercury forms three iodides; a green iodide, Hg_2I_2; a red diiodide, HgI_2; and an intermediate iodide, $HgI.HgI_2$, of a yellow colour, obtained by precipitating mercurous nitrate by means of potassic iodide containing iodine in solution.

(1107) **MERCUROUS IODIDE,** $Hg_2I_2 = 654$, which is a green powder insoluble in water, is easily decomposed by exposure to light, into mercury and the red iodide; the same change is effected by gently heating it with solutions of the soluble iodides or chlorides, or with hydriodic or hydrochloric acid. If heated suddenly it fuses, and may then be sublimed without decomposition; but if the temperature be raised gradually, it is decomposed into the red iodide and metallic mercury. It is easily formed by triturating 5 parts of iodine with 8 of mercury, moistening the mixture with a little alcohol. It

may also be precipitated from a solution of any mercurous salt, by adding to it a solution of potassic iodide, but prepared in this manner it often contains either metallic mercury or mercuric iodide: it may be obtained free from both these impurities by precipitating a solution of 3 parts of mercurous acetate and 6 of sodic pyrophosphate in 30 of water by a solution of 3 parts of potassic iodide in 100 of water.

(1108) **MERCURIC IODIDE,** *Biniodide of mercury;* HgI_2= 454; *Mol. Vol.* [ ]; *Rel. wt.* 227; *Density of Solid,* 6·25; *of Vapour, Theoretic,* 15·708; *Observed,* 15·6; *Comp. in* 100 *parts,* Hg, 44·05; I, 55·95.—This beautiful compound may be prepared by triturating 5 parts of iodine with 4 of mercury, and subliming the mixture, or by precipitating a solution of mercuric chloride by means of a solution of potassic iodide, the precipitate is soluble in an excess of either salt; the precipitate is at first salmon-coloured, but it speedily becomes converted into a brilliant scarlet, crystalline deposit. It may be obtained beautifully crystallized by agitating a weighed quantity of mercury with a comparatively large volume of alcohol and adding the proper proportion of iodine in successive small portions. When heated to about 150° (302° F.) the colour changes from red to yellow, and at about 200° (392° F.) it fuses, and yields a vapour of extraordinary density: as it cools it is deposited in yellow rhombic tables; this yellow colour is again changed to red by mere agitation, or by scratching the crystals. Warington has shown that this change of colour depends upon a change in the molecular constitution of the salt, in consequence of which the rhomboidal crystals are converted into octahedra with a square base. Mercuric iodide is nearly insoluble in water, but it is taken up freely by hot alcohol. It is also dissolved by solutions of many neutral salts of ammonium, as well as by hydrochloric and hydriodic acids. With the soluble electropositive iodides it forms crystalline double salts which are very stable, so that mercuric oxide dissolves readily in a solution of potassic iodide, yielding the double salt, $2KI.HgI_2$, and potassic hydrate. Mercuric iodide is also dissolved easily by solutions of chlorides of the metals of the alkalies, but it does not form crystallizable compounds with these chlorides. A fusible double mercuric chloride and iodide, $HgI_2.HgCl_2$, may be formed; and a soluble crystallizable compound, $HgI_2.2HgCl_2$, may be obtained by saturating a boiling solution of corrosive sublimate with mercuric iodide, and allowing it to crystallize. By adding a mixture of potassic hydrate and ammonia to a solution of mercuric iodide in one of potassic iodide, a brown powder is deposited, to which Nessler assigns the composition, $NHg''_2I.OH_2$ (p. 493). Mercuric

iodide also forms definite compounds with the oxide, and with the sulphide, of the metal.

(1109) **MERCUROUS OXIDE**, or *Suboxide of mercury*; $Hg_2O=416$; *Density*, 10·68; *Comp. in* 100 *parts*, Hg, 96·15; O, 3·85.—Mercury forms two oxides, the black suboxide, Hg_2O, and the red oxide, HgO, both of which form salts with acids: the former, although a powerful saline base, is very unstable when isolated. It is best obtained by triturating finely levigated calomel with a solution of potassic or sodic hydrate, and washing the black precipitate with cold water. It must be allowed to dry spontaneously in a dark place: the oxide so obtained is anhydrous; even when dry, mere exposure to light, or a very gentle heat, is sufficient to convert it into a mixture of red oxide and the metal.

(1110) **MERCURIC OXIDE**, *Nitric oxide* or *Red oxide of mercury*; HgO=216; *Density*, 11·29; *Comp. in* 100 *parts*, Hg, 92·59; O, 7·41.—This oxide may be obtained in red scales by heating metallic mercury at 371° or 426° (700° or 800° F.) in a matrass, but this process is very slow, and not productive; it is more conveniently prepared by decomposing the nitrate by heat, when it has a bright scarlet colour. It may also be thrown down in the form of a yellow powder, by adding a solution of potassic or sodic hydrate to one of mercuric chloride, or mercuric nitrate. The precipitated oxide does not differ in composition from the red crystallized form, but it is more easily acted on than the latter; a cold solution of oxalic acid is without action on the crystallized oxide, but it converts the precipitated oxide into oxalate; the yellow oxide also when boiled with a solution of mercuric chloride is quickly converted into the oxychloride, but this change is very slow with the crystallized variety. The yellow oxide, when boiled with potassic dichromate, yields a basic mercuric chromate, $HgCrO_4.2HgO$, but the crystallized oxide when similarly treated yields a basic salt, with a larger excess of base, $HgCrO_4.3HgO$ (Millon). In short, the crystallized oxide obtained by the direct oxidation of mercury, and the precipitated oxide almost appear to be in different allotropic conditions.

The red oxide becomes nearly black when heated, but recovers its colour on cooling; when ignited, it is decomposed into metallic mercury and oxygen: owing to the volatility of the metal, this oxide may be usefully employed as an oxidizing agent in some analytical operations. This oxide is slightly soluble in water, the solution having an acrid taste, and turning syrup of violets green. It dissolves in fused potassic hydrate without evolution of gas, and if the alkali be nearly saturated with the

oxide, then allowed to cool and extracted with water, a heavy violet crystalline powder is obtained having the composition, $K_2O.HgO$: a similar sodic compound has been prepared. It forms a soluble compound with baryta. With ammonia it produces a yellowish-white insoluble compound, the simplest formula for which is $Hg_2H_5NO_3$; it is possessed of strong basic powers and enters into combination with acids, forming well-defined salts.

(1111) **OXYCHLORIDES OF MERCURY.**—Mercuric dichloride combines with mercuric oxide in several proportions; these compounds are decomposed by the alkalies. One of them is obtained in the form of dark brown insoluble flakes, $3HgO.HgCl_2$, when the dichloride is boiled with mercuric oxide. Another, $2HgO.HgCl_2$, is obtained in blackish scales by acting with a solution of chlorine on mercuric oxide (Thaulow). The mercuric oxychlorides are interesting, from the observations of Millon upon them, which seem to prove the persistence of the allotropic modification in a body after it has entered into combination (*Ann. Chim. Phys.*, 1846, [3], xviii. 333).

The three oxychlorides described by Millon consist of $2HgO.HgCl_2$; $3HgO.HgCl_2$, and $4HgO.HgCl_2$. They may all be produced by the action of potassic carbonate upon a solution of mercuric chloride. The first may be obtained in three different isomeric conditions, the second in two, and the third in three. The action of the carbonates of the alkali-metals upon solutions of mercuric chloride is peculiar. The addition of a solution of the dichloride to a solution of pure *normal* potassic or sodic carbonate is attended with the precipitation of yellow mercuric oxide. If the mercurial solution be added to a solution of an alkaline *hydric carbonate* (bicarbonate), a red oxychloride is formed; and if even a small quantity of the acid-carbonate of the alkali-metal be mixed with a large proportion of normal alkali carbonate, this red precipitate is produced at first. This reaction may serve to distinguish the carbonates from the acid carbonates in solution. If a cold saturated solution of potassic hydric carbonate be added gradually to 8 or 10 times its volume of a cold saturated solution of the dichloride, a light, granular, amorphous precipitate of a bright brick-red colour is formed, $2HgO.HgCl_2$. If the volume of the solution of dichloride be only 3 or 4 times as great as that of the acid-carbonate, a precipitate of similar composition is formed, but it is dense, crystalline, and red, purple, or violet in colour. Both these modifications, when decomposed by potassic hydrate, yield *yellow* mercuric oxide; but if 1 volume of the solution of the hydric carbonate be added to 2 volumes of the solution of the dichloride, stirring briskly, a jet black crystalline precipitate is formed, which also consists of $2HgO.HgCl_2$, but which yields the *red crystalline* mercuric oxide when decomposed by potassic hydrate.

If equal volumes of the solutions be mixed, golden-yellow plates, which gradually become brown or yellowish, are deposited, $3HgO.HgCl_2$. The same body may also be obtained in the amorphous form.

The tetrabasic oxychloride, $4HgO.HgCl_2$, may be obtained by adding a solution of mercuric chloride to a large excess of the solution of the hydric carbonate. Carbonic anhydride gradually escapes, and brown crystalline crusts are deposited: potassic hydrate causes the separation of *red* mercuric oxide from this compound. This oxychloride may also be obtained in the form of a brown amorphous deposit, and in golden-yellow plates; both these varieties yield the *yellow oxide* when decomposed by potassic hydrate. The first two oxychlorides are converted by boiling them with water into the tetrabasic form, which is

deposited from the solution in golden-yellow scales. Other oxychlorides, with 5 and with 6 molecules of mercuric oxide, are described by Roucher (*Ann. Chim. Phys.*, 1849, [3], xxvii. 353).

(1112) **MERCURAMINE,** or *Tetramercurammonic hydrate.*—Th best method of preparing this remarkable base consists in pouring pure solution of ammonia upon yellow precipitated mercuric oxide in bottle which admits of being closed, to prevent the access of carbonic anhy dride from the air; the colour of the oxide becomes paler, and eventually yellowish-white amorphous powder is obtained, which, when washed and drie in a dark place over quicklime, forms the hydrate of the new base, containin $N_2Hg_4H_2O_2.4OH_2$ [$N_2Hg''_4(OH)_2.4OH_2$]. This compound was discovered b Fourcroy and Thénard, but it was first minutely examined by Millon (*Ann Chim. Phys.*, 1846, [3], xviii. 393). In its isolated condition it is very unstable mere exposure to the light decomposes it. When triturated in a mortar, i produces a series of detonations. If dried *in vacuo* over sulphuric acid, it lose $2OH_2$; and between 100° (212° F.), and 130° (266° F.), a third molecule o water is expelled: it then becomes dark brown and is permanent in the air, con taining $N_2Hg_4H_2O_2.OH_2$. According to Weyl (*Pog. Ann.*, 1864, cxxi. 601 cxxxi. 1867, 524), the hydrate prepared by passing dry ammonia over pre cipitated mercuric oxide is $N_2Hg_4H_2O_2.2OH_2$, which at 80° (176° F.), lose water and becomes $N_2Hg_4H_2O_2$, and at 100° (212° F.), leaves the anhydrou oxide, N_2Hg_4O.

Mercuramine is not soluble either in water or in alcohol, but it is a powerfu base, its hydrate, $N_2Hg_4H_2O_2.4OH_2$, absorbs carbonic anhydride from the ai almost as rapidly as slaked lime, and it decomposes solutions of the salts of am monium and combines with the acid. Definite salts with sulphuric, nitric, oxali carbonic, hydrochloric, and various other acids, have been formed. On th addition of sodic or potassic hydrate to the solutions of these salts, the hydrat of the base is precipitated. The formula of the sulphate is $N_2Hg_4SO_4.2OH_2$ that of the chloride is $N_2Hg_4Cl_2.2OH_2$; the latter salt is obtained as a yello precipitate on adding a solution of mercuric chloride to a solution of ammoni in excess, and washing the precipitate with boiling water (1104).

(1113) **MERCURIC SULPHIDE,** *Sulphide of mercury,* o *Cinnabar;* HgS=232; *Density of Vapour, Theoretic,* 5·351 *Observed,* 5·51; *of Solid,* 8·2; *Mol. Vol.* [ ]; * *Rel. wt* 77·333; *Comp. in* 100 *parts,* Hg, 86·21 S, 13·79.—There is bu one sulphide of this metal, HgS; the black precipitate, obtained on passing a current of sulphuretted hydrogen through a solution of a mercurous salt and formerly supposed to be mercurous sul phide, being merely a mixture of metallic mercury and mercuri sulphide (Barfoed, *Bull. Soc. Chem.*, [2], iii. 183). *Ethiop's mineral,* prepared by triturating 8 parts of moistened sulphu with 100 of mercury, is probably also a mixture. It is decom posed by nitric acid; and if the dry sulphide be sublimed, it i converted into cinnabar and metallic mercury.

* The vapour volume of this compound is anomalous, the three volumes o vapour having been united without condensation, instead of being, as usual, re duced to two volumes.

Mercuric sulphide constitutes the most abundant ore of mercury. It occurs sometimes crystallized in hexahedral prisms, but more usually as a fibrous or amorphous mass, and is a product of considerable importance in the arts, forming the pigment known under the name of *vermilion*. Some portions of the native cinnabar are of a sufficiently delicate colour to be employed after mere levigation, but it is usually prepared artificially. In Holland, this manufacture is carried on to a considerable extent. The process adopted consists in triturating sulphur with about 6 times its weight of mercury, aiding the action by a gentle heat. The black mass thus obtained is thrown (in successive portions, to prevent too rapid an action) into tall earthen pots, the lower parts of which have been previously brought to a red heat; the aperture at top is closed with a smooth iron plate, which is replaced by another as soon as a sufficient quantity of cinnabar has collected on it; fresh materials being introduced into the pot from time to time; the cinnabar after being detached from the plates is levigated with water, and the fine powder thus obtained is sold as vermilion; an excess of sulphur is to be avoided, as it impairs the brilliancy of the colour. Cinnabar sublimes before undergoing fusion, and forms a yellowish-brown vapour.

Vermilion may also be prepared in the wet way, but the process is tedious, and less certain. The Chinese vermilion is supposed by some chemists to be prepared by the humid process. In order to produce vermilion by this means, Firmenich recommends the mercury to be subjected to the action of pure dipotassic pentasulphide, K_2S_5, in the following manner:—10 parts of mercury are to be agitated for 3 or 4 hours, with 2 parts of sulphur and $4\frac{1}{2}$ of a saturated solution of dipotassic pentasulphide; at the end of which time the mixture becomes of a dark brown colour. It is maintained for 3 or 4 days at a temperature of from 45° to 50° (113° to 122° F.) with occasional agitation; it is next drained upon a filter, and afterwards digested with sodic hydrate to remove the excess of sulphur; it is thus obtained of a bright scarlet colour, and must then be thoroughly washed with cold water and dried (*Chem. News*, 1862, v. 247). It, however, contains metallic mercury which may be removed by treatment first with nitric acid, then with ammonia, and again with nitric acid.

Cinnabar may also be obtained by adding a solution of mercuric chloride to dilute ammonia, and then a solution of sodium thiosulphate, rather more than sufficient to dissolve the precipitate. On warming the solution, cinnabar separates.

Mercuric sulphide is thrown down as a black precipitate by passing sulphuretted hydrogen through solutions of the mercuric salts: when dried and sublimed in vessels from which the air is excluded, it assumes its ordinary red colour. By simple heating it becomes dark brown, and at a still higher temperature nearly black, but recovers its red colour on cooling. When heated in the open air, the sulphur burns off, and metallic mercury is

liberated. It is upon this circumstance that the ordinary process for extracting the metal is founded. The pure acids are nearly without action upon cinnabar, but it is oxidized and dissolved by aqua regia. The alkaline hydrates in solution do not decompose it, but if ignited with them in the dry state, a sulphate and sulphide of the alkali-metal are formed, and metallic mercury sublimes; $4HgS + 8KHO = 4Hg + K_2SO_4 + 3K_2S + 4OH_2$. It is also decomposed if heated with metals which, like iron, zinc, and copper, have a powerful attraction for sulphur; or even at the ordinary temperature, in presence of water. Mercuric sulphide possesses the property of uniting with other metallic sulphides, and is soluble in a solution containing sodic sulphide and hydrate, forming an orange-red solution; it also combines with the nitrate, the chloride, the iodide, and some other mercuric salts, forming peculiar compounds, which are produced by the action of a small proportion of sulphuretted hydrogen upon the solution of these salts, and the production of which causes the first portions of the precipitate occasioned in them by the gas to appear white. When digested with cupric chloride and hydrochloric acid, mercuric sulphide yields a brilliant orange-yellow powder, having the composition, $Hg_2S_2.Cu_2Cl_2$.

(1114) **Nitride (?) of Mercury.**—Plantamour states, that by passing a current of dry ammoniacal gas over the dried yellow mercuric oxide precipitated from its salts by an alkali, so long as the gas is absorbed, and then heating the dark brown mass cautiously at a temperature not exceeding 150° (302° F.), so long as water is formed, an anhydrous powder of a brown colour is produced. It detonates powerfully when heated or struck: the acids decompose it, forming salts of ammonium and mercury. It is probably identical with a compound obtained by Weyl by the long-continued heating of the anhydrous oxide, N_2Hg_4O, (1112) in ammonia.

(1115) **MERCURIC SULPHATE,** or *Sulphate of mercury;* $HgSO_4 = 296$; *Density,* 6·466.—When 2 parts of mercury are heated gently with 3 of sulphuric acid, sulphurous anhydride is evolved, and mercurous sulphate is produced; but if the heat be increased and the distillation be carried to dryness, mercuric sulphate is formed; sulphurous anhydride being evolved, whilst the mercury takes oxygen from the sulphuric acid; $Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2OH_2$. It is a white crystalline powder, which is soluble in a solution of common salt, but is decomposed by pure water into an insoluble, yellow, basic salt, called *turpeth mineral* ($HgSO_4.2HgO$; *density* 8·319), and a soluble acid salt, which crystallizes in deliquescent needles; the yellow basic salt is formed more rapidly if the sulphate be washed with boiling water. The normal sulphate, when treated with an excess of ammonia, yields

mercuramine sulphate. The normal sulphate unites with ammonic sulphate, forming a crystallizable double salt.

(1116) **NITRATES OF MERCURY.**—Mercury forms a larger number of nitrates than any other metal. The conditions of temperature, and dilution of acid necessary to insure the production of each compound, vary but little in each case, and their accurate analysis is attended with some difficulty. Different chemists vary somewhat in their statements of the results which they have obtained. The *normal subnitrate,* or *mercurous nitrate,* $(Hg_2)''2NO_3.2OH_2$, is obtained by digesting metallic mercury in an excess of nitric acid diluted with 4 or 5 times its bulk of water; it crystallizes, in short, transparent, somewhat efflorescent prisms (or in rhombic plates; Gerhardt); water decomposes it into a yellow insoluble dibasic salt, $(Hg_2)''2NO_3.Hg_2O.OH_2$, or $2Hg_2O.N_2O_5.OH_2$, and a soluble acid one. A soluble subnitrate, which is often mistaken for the normal salt, crystallizes in large, transparent, colourless prisms, $3(Hg_2)''2NO_3.(Hg_2)''O.OH_2$, or $4Hg_2O.3N_2O_5.OH_2$, and is obtained by digesting an excess of mercury in dilute nitric acid. De Marignac finds that by boiling the mother-liquors of the preceding salts with an excess of mercury for several hours, doubly oblique, rhombic, colourless prisms are deposited, to which he assigns the composition, $3(Hg_2)''2NO_3.2[(Hg_2)''O.OH_2]$, or $5Hg_2O.3N_2O_5.2OH_2$. Other subnitrates also appear to exist. These various basic nitrates may be distinguished from the normal salt by triturating them with sodic chloride; they then become grey, calomel being formed, and black mercurous oxide separated; the normal salt does not change colour under these circumstances.

A normal *mercuric nitrate,* $2Hg''2NO_3.OH_2$, is slowly formed in voluminous crystals, by dissolving mercuric oxide in an excess of nitric acid, and evaporating the liquid until it assumes a syrupy consistence. Another nitrate, $Hg2NO_3.HgO.2OH_2$, or $2HgO.N_2O_5.2OH_2$, is deposited in acicular crystals from a boiling solution of mercury in excess of nitric acid; but it is obtained with greater certainty by saturating nitric acid of density 1·4, diluted with an equal bulk of water, with mercuric oxide. The solutions of both these salts are decomposed when freely diluted with water, and a yellow insoluble basic nitrate, $Hg2NO_3\ 2HgO.OH_2$, or $3HgO.N_2O_5.OH_2$, is precipitated: by long-continued washing with hot water, the whole of the nitric acid is removed from this basic salt, and mercuric oxide is left. Solutions of the mercuric nitrates, when digested with an excess of the metal, are converted into mercurous nitrates.

(1117) **Characters of the Salts of Mercury.**—Most of the salts of mercury are colourless, but some of the basic mercuric salts are yellow. The following characters are common to both the mercurous and mercuric salts. The soluble compounds have an acrid, nauseous, metallic taste: in large doses they act as irritant poisons. All the mercurial compounds are volatilized by heat. If a small quantity of any of the dry salts of this metal be placed at the bottom of a tube of the diameter of a quill, and be covered to the depth of 1 inch ($25^{mm.}$) with a layer of dried sodic or potassic carbonate, the mercury sublimes in the form of minute globules, on heating the upper part of the layer of the carbonate to redness, and driving the vapour of the mercurial compound slowly through it.

The presence of mercury, when in solution, may be detected by placing a small strip of zinc, round which a thin strip of gold foil is twisted, in a portion of the liquid to be tested. The mercury will be deposited by voltaic action in the form of a white stain upon the gold. This stain will disappear on heating the gold to redness. The salts of mercury, whether soluble or insoluble, are all reduced to the metallic state when heated with a solution of *stannous chloride*. A strip of metallic *copper* becomes coated with a white amalgam, if rubbed with a solution containing mercury. This test may be employed for detecting the presence of mercury in solution in a manner similar to that proposed by Reinsch for arsenic (995), a sublimate of mercury in distinct globules being obtained by heating the coated slip in a small tube.

1.—*Mercurous salts* are characterized, when in solution, by yielding with solutions of *potassic, sodic,* or *calcic hydrates,* a black precipitate of mercurous oxide. *Potassic ferrocyanide* gives a white precipitate. Both *sulphuretted hydrogen* and *ammonic hydric sulphide* yield a black precipitate. *Hydrochloric acid* and solutions of the *chlorides* cause a white precipitate of calomel, which is soluble in hot concentrated nitric acid, and in chlorine water; it is blackened by the addition of an excess of ammonia. *Potassic iodide* gives a green mercurous iodide, and *potassic chromate* a bright red basic mercurous chromate.

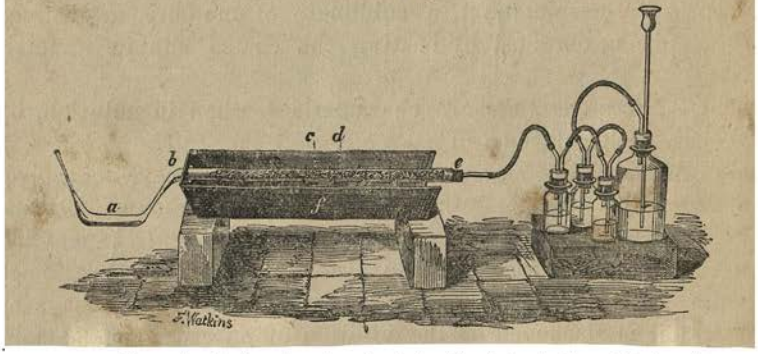
2.—*Mercuric salts,* when in solution, yield with solutions of *potassic, sodic,* or *calcic hydrates,* a bright yellow precipitate of mercuric oxide; with *ammonia,* a white precipitate; with *normal potassic carbonate,* a yellow precipitate of oxide; with *potassic hydric carbonate,* a red precipitate of mercuric oxychloride (1111): all these precipitates are soluble in hydrochloric acid. *Ammonic*

hydric sulphide gives a black precipitate; and *sulphuretted hydrogen*, a dirty white precipitate, which passes through red into black; it is insoluble in nitric or in hydrochloric acid: this sulphide is insoluble in the sulphides of the alkali-metals unless an excess of alkali be present, in which case the precipitate is gradually dissolved. *Potassic iodide* precipitates a salmon-coloured mercuric iodide, which quickly becomes of a brilliant scarlet: this precipitate is soluble in excess both of potassic iodide, and of mercuric chloride. *Hydrochloric acid* and solutions of the *chlorides* give no precipitate with the mercuric salts. *Potassic ferrocyanide* gives a white precipitate, which gradually becomes blue, while mercuric cyanide is formed in the solution.

(1118) **Estimation of Mercury.**—Mercury is usually estimated in the metallic form. If the solution contain neither lead nor silver, metallic mercury may be precipitated by the addition of stannous chloride, acidulated with hydrochloric acid: the metal must be collected on a weighed filter, and dried *in vacuo* over sulphuric acid.

When the compound is in the solid form, Millon recommends the following plan for effecting the decomposition of the combinations of mercury and for collecting the metal:—A hard glass tube, 18 or 20 inches (45 or 50$^{cm.}$) long, such as is used in the analysis of organic compounds, is drawn out in the manner represented in fig. 365, and at *a* a small bulb is formed for the reception of the

FIG. 365.



mercury; a plug of asbestos is placed at *b*; the tube is then filled as far as *c* with fragments of quicklime, and the mercurial compound, in quantity varying from 15 to 45 grains (1 to 3 grams), is introduced between *c* and *d*, and the tube is filled up with fragments of lime. If nitric acid be present in the compound, metallic copper must be substituted for quicklime. The extremity, *e*, is connected with an apparatus, *g*, which supplies a steady current of pure dry hydrogen—the tube being placed in a sheet-iron furnace, *f*, whilst the receiver, *a*, projects beyond the furnace, and is kept cool. As soon as the apparatus is filled with the gas, lighted charcoal is applied to the first third of the tube between *b* and *c*, and when it is at a full red heat, glowing charcoal is very gradually

added until the whole length of the tube is red hot; the mercury collects in *a*, and the water, which is at first condensed, is gradually removed by the current of dry hydrogen. When the operation is over, the narrow portion of the tube between *a* and *b* is cut with a file, and the detached portion *a*, with its contents, is weighed: the mercury is emptied, the bulb cleansed with nitric acid and water, then dried, and weighed a second time; the difference gives the weight of the condensed mercury.

§ II. SILVER: (Argentum) Ag′ = 108.

(1119) **SILVER**: *Density*, 10·53; *Fusing-pt.* 916° (1681° F.).—This metal has been known from the earliest ages, and has always been prized for its rarity, and its brilliant lustre. It has a white colour with a tinge of red; in hardness it is intermediate between copper and gold, and it is endowed with considerable tenacity; it may be hammered into very thin leaves, and admits of being drawn into very fine wire. When very thin it transmits light of a bluish-green colour; in somewhat thicker layers it is yellow. By repeated heatings, however, this metal assumes a crystalline texture, and it then becomes brittle. It crystallizes in forms belonging to the regular system. Silver fuses at 916° (1681° F.), and on cooling expands forcibly at the moment of solidification. It is not sensibly volatilized if heated in closed vessels, but a silver wire is dispersed in greenish vapours when a very powerful electrical discharge is sent through it; when heated before the oxyhydrogen jet on lime (1167, fig. 375) it may be made to boil, and give off vapours which become oxidized in the current of gas if it contains an excess of oxygen.

In his elaborate researches upon the combining proportions of the elements, Stas has availed himself of the volatility of silver in the heat of the oxyhydrogen jet to obtain the metal in a state of absolute purity. For this purpose in a block of lime, from white marble, 25 or 30$^{cm.}$ long, 10$^{cm.}$ high, and as many in thickness, a cavity 3$^{cm.}$ in diameter, and 2$^{cm.}$ deep, was drilled, and connected with a sloping channel of 3$^{cm.}$ wide, and 5$^{mm.}$ deep, which acted as a condenser to the silver: the channel terminated in a cavity for the reception of the distilled metal. A cover of lime was fitted to this sort of still, and 50 grams of silver were introduced into the cavity, heated by the oxyhydrogen jet; in this way the whole of the silver was distilled in from 10 to 15 minutes, but a good deal escaped condensation. The density of distilled silver is 10·575, but Dumas has found (*Compt. Rend.*, 1878, lxxxvi. 65) that it still contains oxygen, which it only gives up when strongly heated in a vacuum: if fused in a vacuum after all the oxygen has been removed, it was found to have a density of 10·512 when solid.

Silver is an excellent conductor both of heat and electricity, and is superior in these respects to any known substance. Silver is not oxidized by exposure to the atmosphere at any temperature. Pure silver, however, when melted, absorbs oxygen mechanically,

to an extent amounting, it is said, to 22 times the bulk of the metal, but the gas is given off almost entirely at the moment of solidification: if a mass of melted silver be allowed to cool suddenly, the outer crust becomes solidified, and when the interior portion assumes the solid condition it ruptures the crust; small tubes or globules of melted metal are then forcibly expelled by the escaping oxygen, aided by the sudden expansion which the silver undergoes in the act of solidification. This phenomenon, which is termed the *spitting* of the globule, is entirely prevented by the presence of 1 or 2 per cent. of copper. Silver combines slowly with chlorine, bromine, and iodine: if fused with phosphorus the two bodies enter into combination. Silver has a powerful attraction for sulphur; by long exposure to the air the metal becomes superficially blackened or tarnished, from the formation of a thin film of sulphide upon its surface; this is due to the decomposing action of the metal upon the small portion of sulphuretted hydrogen which is constantly floating in the air, especially in large towns. This tarnish is readily removed by means of a solution of potassic cyanide. Commercial silver occasionally contains selenium derived from the sulphuric acid used in the refining process.

The best solvent for silver is nitric acid, which, if diluted with an equal bulk of water, acts upon the metal with great violence, dissolving it rapidly and evolving nitric oxide, whilst argentic nitrate is formed. Hydrochloric acid acts upon it but slightly. Aqua regia attacks it more rapidly. Dilute hydriodic acid attacks it with evolution of hydrogen. Boiling oil of vitriol dissolves it with evolution of sulphurous anhydride. If common salt be fused in a silver dish, or if it be moistened and left in contact with silver, it gradually corrodes it; soda being formed by the absorption of oxygen from the air, whilst the liberated chlorine attacks the silver. Neither the alkaline hydrates nor nitrates exert any considerable action upon it, whether in solution or when fused, hence crucibles for the fusion of refractory minerals with potassic hydrate are commonly made of this metal.

The value of silver as a medium of exchange has caused it to be adopted as such by all civilized nations from the earliest ages of the world. When alloyed with certain proportions of copper it is used for the current coin of the realm, and for the various articles of plate. From its superior power of reflecting light, it forms the best surface for the reflectors employed in light-houses at sea.

(1120) **Extraction of Silver from its Ores.**—Silver is frequently met with pure in the native state, either in fibrous masses, or crystallized in cubes or octahedra, or sometimes combined with gold, mercury, or antimony, or in slender filaments in some samples of galena; generally, however, it is found in combination with sulphur, mixed with the sulphides of lead, antimony, copper, and iron. The mines of Peru and Mexico are the most extensive sources of silver. In Europe, those of Kongsberg in Norway, and of Schneeberg and Freyberg in Saxony, are celebrated: there are also numerous other mines from which smaller quantities are obtained. The ores of silver occur usually among the primitive rocks, frequently in calcareous veins, traversing either gneiss, or slaty and micaceous deposits. Plumbic sulphide is nearly always accompanied by small quantities of argentic sulphide, and a considerable quantity of silver is extracted during the refining of lead by Pattinson's process (1058), as well as by cupellation (1059).

At Freyberg, silver is for the most part obtained from the sulphide by the method of *amalgamation*. The plumbiferous ores are in this case rejected, as they are not adapted to this method of proceeding, but are treated in the manner already described when speaking of lead. The ores are usually sorted, so that they shall contain about 0·24 parts of silver in 100, or about 80 ounces per ton of ore, and not more than 1 per cent. of copper; the proportion of iron pyrites is not allowed to exceed, or greatly to fall short of 35 per cent. The metalliferous mass, after it has been reduced to a coarse powder, is mixed with a tenth of its weight of common salt, and sifted, to insure its intimate incorporation: it is then roasted, at first at a low red heat; during this operation, care is taken to keep the mixture constantly stirred, in order as far as possible to prevent it from concreting into lumps. Meantime arsenic and antimony are expelled in dense white fumes of arsenious and antimonious sesquioxide, and the sulphides of the other metals are partially oxidized; the silver unites with chlorine derived from the salt, the sodium of which combines with oxygen and sulphur, so that argentic chloride and sodic sulphate are formed; the copper and the iron are changed partly into sulphates, partly into chlorides, and partly into oxides, as is shown in the subjoined equations:

$$Ag_2S + 2NaCl + 2O_2 = 2AgCl + Na_2SO_4;$$
$$CuS + 2O_2 = CuSO_4;$$
$$2CuS + 4NaCl + 4O_2 = Cu_2Cl_2 + Cl_2 + 2Na_2SO_4;$$
$$2FeS_2 + 6NaCl + 7O_2 = Fe_2Cl_6 + 3Na_2SO_4 + SO_2.$$

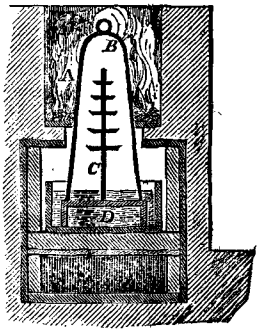
During the early stages of this operation, fumes of sulphurous anhydride are given off abundantly, and the roasting is continued until these have in a great measure given place to those of chlorine and ferric chloride. A charge of 4½ cwt. requires 6 hours roasting. The roasted mass is now raked out of the furnace, and allowed to cool: it is next sifted in order to separate the lumps, which are powdered and again submitted to the same operation. About 85 per cent. of the silver is thus converted into chloride at the first roasting. The portions which have passed through the sieve are ground to powder, and passed through a bolting sieve to procure a very fine metal. The powder is next placed, with from a third to half its weight of water, in large casks, which are charged with about 500 kilos., or half a ton of the ore. These casks are caused to revolve upon horizontal axes, about 20 times per minute; 50 kilos., or about 1 cwt. of scrap wrought iron is then introduced into each cask, and after the lapse of an hour, 250 kilos., or about 5 cwt. of mercury is added, after which the casks are again made to revolve for about 20 hours; during this operation a slight rise of temperature is observed. The powder when placed in the casks consists principally of argentic chloride mixed with large quantities of cupric sulphate and cuprous chloride, as well as of ferric chloride, with a variable proportion of the oxides of copper and iron. The object of agitating the mixture with the iron before adding the mercury is to reduce the ferric chloride to ferrous chloride in the first instance; if this precaution were not taken, the mercury would be partly converted into calomel, which would not subsequently be decomposed, and would thus be lost: the excess of iron afterwards removes the chlorine from the argentic chloride and cuprous chloride, and the sulphuric acid from the copper:

$$Fe_2Cl_6 + Fe = 3FeCl_2; \qquad 2AgCl + Fe = FeCl_2 + Ag_2.$$
$$Cu_2Cl_2 + Fe = FeCl_2 + 2Cu; \qquad CuSO_4 + Fe = FeSO_4 + Cu.$$

The presence of the mercury favours this reaction, by establishing a voltaic current, and the silver and copper thus set at liberty unite immediately with the mercury, forming a liquid amalgam. At the expiration of 18 or 20 hours the casks are filled up with water, and are set again in motion for a couple of hours to allow the amalgam to be washed out of the spent materials, after which the fluid amalgam is drawn off into sacks of ticking; these sacks form a kind of rude filter, through which the greater part of the mercury runs into a stone trough, leaving behind it a soft solid containing from 15 to 17 per cent. of silver. The mud in the

casks is again submitted to washing; the residual amalgam subsides, owing to its greater density, and the lighter portions are rejected. The filtered part of the mercury, which retains a small quantity of silver, is used again for the amalgamation of a fresh portion of ore. The silver in the solid amalgam has now to be separated from the remaining mercury; for this purpose it is placed in trays, supported on a tripod, C, fig. 366, under a large distillatory iron bell, B, round the upper part of which a fire, A, is lighted; the bell and its contents are thus brought to a red heat, by which means the mercury is driven off; its vapour descends, and is condensed in the water contained in the vessel, D. The operation is generally performed on 250 kilos., or about 5 cwt. of amalgam at a time, and occupies 8 hours. The residual spongy mass of silver and copper is then fused and cast into ingots, which in the Saxon mines usually contain about 70 per cent. of silver and 28 of copper.

Fig. 366.



In the process of amalgamation a considerable loss of mercury occurs from its becoming very finely divided, or, as it is termed, the 'flouring' of the mercury. This may be prevented to a considerable extent by employing mercury containing about 1 or 2 per cent. of sodium, as suggested by Crookes.

An improvement upon this process has been introduced by Augustin, who dispenses with the use of mercury altogether. After the ore has been roasted first by itself, and again a second time with sodic chloride, it is digested in a concentrated solution of common salt; such a solution dissolves argentic chloride readily: a dilute solution of sodic chloride exerts little or no solvent action; and the concentrated liquid when diluted deposits the argentic chloride which it had previously dissolved. In practice it is found better, instead of diluting the liquid, to digest it with metallic copper; the chloride of silver is decomposed, chloride of copper is formed and dissolved, whilst metallic silver is precipitated. The presence of cupric chloride in the solution of the sodic chloride does not prevent the liquid from being employed again for the extraction of chloride of silver from fresh portions of the roasted ore.

Another important improvement in the operation was made by Ziervogel. He avoids the preparation of argentic chloride entirely, and merely roasts the sulphurous ores in such a manner that the sulphates of iron and copper are completely decomposed, whilst the argentic sulphate, which withstands a much higher temperature, remains undecomposed in the mass. In this operation the powdered ore is roasted until it gives off no odour of sulphurous anhydride, and yields no sensible amount of cupric sulphate when thrown red hot into water: boiling water then dissolves out the argentic sulphate, but the oxides of copper and iron remain undissolved. The silver is precipitated from the liquid by means of

metallic copper as before. A small quantity of silver is still retained in the undissolved residue, from which it may be advantageously extracted by the method of Augustin. Both these processes have been patented and practised on a large scale in England.

Percy has suggested the use of sodic thiosulphate (hyposulphite of soda) as a solvent for argentic chloride. The mineral after roasting with sodic chloride is washed first with hot and then with cold water, and is afterwards digested in a dilute solution of the alkaline thiosulphate, which dissolves the argentic chloride; from this solution the silver is precipitated as sulphide, by means of sodic sulphide, whilst sodic thiosulphate is reproduced as before.

(1121) **American Process of Amalgamation.**—In the mining districts of Mexico and Chili, where fuel is expensive, and where ores are often worked of a much poorer description than in Europe, the process of amalgamation is different. A good deal of the silver occurs in the native state, so that it unites directly with the mercury. The mineral after being stamped and ground to a fine powder in mills, is moistened with water, and mingled with from 1 to 5 per cent. of salt; the mixing being effected by the trampling of horses during 6 or 8 hours. The ore thus blended with the salt is allowed to remain undisturbed for some days, after which an addition of $\frac{1}{200}$ or $\frac{1}{100}$ of its weight of what is technically termed *magistral* is made. This substance consists of roasted copper pyrites, and contains about 10 per cent. of cupric sulphate, the remainder being ferrous sulphate and other impurities; mercury, to the extent of twice the quantity of silver that the ore contains, is then added, the mixture being effected, as before, by the trampling of horses. It is again allowed to rest for 16 or 20 days: during this period a considerable portion of the silver becomes united with the mercury, forming a hard, brilliant amalgam, and at the same time a large quantity of calomel is formed. Another equal quantity of mercury is added, and a still longer interval of rest is allowed; then a third dose of mercury to the same extent follows; by this last addition a fluid amalgam is obtained, which is separated by washing, then filtered, and the mercury expelled from the silver by distillation. The quantity of mercury consumed in this process varies from 130 to 150 parts for each 100 parts of silver extracted, great waste being incurred owing to the formation of calomel, which is not recovered. It is calculated that up to the close of the last century, 6 million cwt. of mercury had thus been lost by the processes adopted in the American mines in the course of 200 years.*

* Dumas proposes to recover this mercury by treating the washed residue with a quantity of chloride of lime or sodic nitrate, proportioned to the mercury

The theory of this operation is rather obscure. The cupric sulphate of the magistral, and the sodic chloride decompose each other, cupric chloride and sodic sulphate being formed. Cupric chloride, in the presence of metallic silver, is converted into cuprous chloride, whilst argentic chloride is produced; $2Cu''Cl_2 + Ag_2 = (Cu_2)''Cl_2 + 2AgCl$. When cuprous chloride, with excess of common salt and water, is brought into contact with argentic sulphide, the cuprous chloride is dissolved by the solution of sodic chloride; this solution of cuprous chloride decomposes the argentic sulphide, and is converted into cuprous sulphide, whilst argentic chloride is formed; $(Cu_2)''Cl_2 + Ag_2S = (Cu_2)''S + 2AgCl$. The excess of salt dissolves the argentic chloride, and the addition of mercury decomposes this dissolved chloride; calomel is formed, and an amalgam of silver is obtained; $2AgCl + 2Hg = Hg_2Cl_2 + Ag_2$. If too much magistral be added, an excess of cupric chloride, $CuCl_2$, is produced; this state of the mixture is easily perceived, for in such a case the globules of mercury in the mixture appear to be too minutely divided; the addition of lime then becomes necessary in order to decompose the excess of cupric chloride, otherwise this salt would reconvert the silver into chloride, and the mercury into calomel.

(1122) **Separation of Silver from Copper by Liquation.**—It occasionally happens that a copper ore contains a considerable amount of silver, which, under certain circumstances, it may be desirable to extract by the process of *liquation*. For this purpose the copper, having been brought to the stage of blister copper (1033), is melted with from 3 to 4 times its weight of lead: the mixture is cast into circular ingots in iron moulds, which suddenly cool the alloy, and cause it to solidify before the copper and lead have time to separate from each other. The proportion of lead should not be less than 500 times that of the silver in the mass. These cakes are then subjected to the action of a moderate heat; the lead, combined with nearly all the silver, and a small proportion only of copper, gradually runs from the mass, leaving a spongy residue, consisting chiefly of copper, but still retaining a small proportion of lead. The argentiferous lead is afterwards subjected to the process of cupellation, whilst the copper from which it has been separated is subjected to a careful roasting in order to oxidize the remainder of the lead, and it is then refined much in the usual manner.

(1123) **Plating and Silvering.**—Silver is frequently employed to give a coating to the surface of less expensive metals. Goods so prepared are said to be *plated*, if the proportion of silver be considerable, and *silvered* if it be small. Plating on copper is

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they contain, then adding hydrochloric acid in slight excess; the calomel would thus be converted into corrosive sublimate. This is to be removed by methodical washing, and the mercury precipitated by copper. The solution of copper thus obtained would furnish the magistral required for a new operation upon fresh ore.

effected by polishing the upper surface of the ingot which is to be plated, and then placing upon it a bright slip of silver, the superficial area of which is a little smaller than that of the copper which it is intended to cover: the thickness of the plate of silver in proportion to that of the copper varies with the value of the goods. The compound ingot is then exposed to a temperature just below the fusing-point of the silver, which softens at its surface. By hammering or rolling out at this high heat, the two metals are *sweated* together, as it is termed, and become inseparably united. No solder is used in this process, but a small portion of powdered borax is placed round the edge of the silver to prevent the surface of the copper from becoming oxidized. The ingot is then rolled until it is reduced to the required degree of tenuity.

Plating on steel is effected rather differently. The article (a dessert knife, for example) having been first brought to the shape required, is tinned upon its surface, and then a slip of silver foil is soldered on. After the silver has been attached, the superfluous portion is removed, and the article is finished up and polished.

These methods of plating have, however, been to a great extent superseded by the process of electro-plating, in which the silver is deposited upon the surface by voltaic action (295).

Silvering may be effected either by the *wet* or by the *dry* method. The wet method is usually adopted for such purposes as the silvering of thermometer scales. It is generally executed either on brass or on copper: the surface of these metals is cleaned by *dipping*, or momentary immersion of the articles in nitric acid, to remove the film of oxide which always forms from exposure to the atmosphere, even for a few hours. After rinsing them in water to remove the nitric acid, they are rubbed over with a mixture of 100 parts of cream of tartar, 10 of argentic chloride, and 1 part of corrosive sublimate. The mercury appears to act as a kind of solder to the silver, the copper combining with the chlorine both of the chloride of silver and of the sublimate; the surface is afterwards polished.

Dry silvering is effected by dissolving a certain quantity of silver in mercury; the 'dipped' articles are agitated with a portion of this amalgam, which thus becomes diffused uniformly over the surface. By the application of heat the mercury is expelled, leaving a very thin film of silver behind: on polishing the trinkets a bright silvered surface is obtained.

(1124) **Silvering of Mirrors.**—Some of the salts of silver when rendered slightly ammoniacal and mixed with certain organic solutions, such as aldehyde or grape-sugar, are reduced to the metallic state, the silver being deposited upon the surfaces of glass vessels in which the experiment is made, in the form of a brilliant, adhering, mirror-like coating. Mr. Drayton some years ago proposed to apply this operation to the silvering of mirrors upon a large scale, as the coating adapts itself not only to flat surfaces, but to those also which are curved, or cut into patterns. Mirrors were formerly silvered at Paris by the following process:—40 grams of pure neutral argentic nitrate are dissolved in 80 c. c. of water. To this solution are added: 1st, 5 c. c. of a liquor prepared from 25 parts of distilled water, 10 of ammonic sesquicarbonate, and 10 of a solution of ammonia of density 0·980; 2nd, 2 c. c. of a solution of ammonia of density 0·980; and 3rd, 120 grams of alcohol of density 0·850. The mixture is left at rest to become clear. The liquid is decanted or filtered, and a mixture of equal parts of alcohol (density 0·850) and oil of cassia is added, in the proportion of 1 part of this *essence of cassia* to 15 parts of the solution of silver; the mixture is agitated and left to settle for several hours, after which it is filtered. Just before pouring it upon the glass to be silvered, it is mixed with $\frac{1}{78}$ of its bulk of *essence of cloves* (composed of 1 part of oil of cloves, and 3 of alcohol, density 0·850). The glass, having been thoroughly cleansed, is covered with the silvering liquid, and warmed to about 40° (104° F.), at which temperature it is maintained for two or three hours: the liquid is then decanted, and may be employed for silvering other glasses. The deposit of silver upon the glass is washed, dried, and then varnished (Pelouze and Fremy, *Traité de Chimie*, 2nd ed., iii. 347).

An alcoholic solution of grape-sugar produces the same result, if substituted for the oils of cassia and cloves, but the deposit occurs much more slowly. Liebig's method of reducing an ammoniacal solution of argentic nitrate alkalized with sodic or potassic hydrate, by means of milk-sugar, at ordinary temperatures, has been successfully applied by Steinheil, in the following manner, to the silvering of mirrors for telescopes (*Ann. Chem. Pharm.*, 1856, xcviii. 132):—Dissolve in 200 measures of water $\frac{1}{20}$ of its weight of pure argentic nitrate, and add to the liquid a solution of ammonia in quantity just sufficient to redissolve the argentic oxide which is at first precipitated; add to this solution 450 measures of a solution of sodic hydrate (density 1·035) free from chloride, and immediately redissolve the dark-brown precipitate thus produced by the cautious addition of ammonia, after which dilute the liquid with water to 1450 measures; then add a solution of argentic nitrate until a decided permanent grey precipitate is formed, and finally pour in water until the mixture occupies exactly 1500 measures: then leave it to stand, and decant the clear liquid. Immediately before the solution is to be used, it is to be mixed with an eighth or a tenth of its volume of a solution of milk-sugar in ten times its weight of water. The solution is to be placed in a shallow vessel, and the glass to be silvered supported just at the surface of the liquid: a beautiful coherent film of silver is deposited upon the under surface of the glass, and a copious precipitation of silver occurs upon the sides of the vessel.

A very good method of silvering glass is that of Petit-Jean (*Chem. Gaz.*, 1856, p. 319), in which an ammoniacal solution of tartrate of silver is employed at a gentle heat: Böttger (*Bull. Soc. Chem.*, 1864, ii. 302) dissolves 1 dram of argentic nitrate in 1 oz. of water, adds ammonia until the precipitate at first produced is nearly redissolved, adds 12 oz. water and filters. The reducing solution is prepared by pouring a solution of 1 dram of argentic nitrate in 1 oz. of water into a boiling solution of 48 grains of sodic potassic tartrate in 48 oz.

water, boiling for 10 minutes, and filtering when cold. A mixture of equal volumes of these solutions deposits a film of silver in the course of 10 minutes: if a thicker film is desired the operation may be repeated with a fresh quantity of solution. Another process for silvering glass specula is given in *Chem. News* (1866, xiv. 214).

By using a solution of auric ammonic citrate, it is easy to gild upon glass; and in a similar way the surface may be platinized if a solution of sodic platinic tartrate be employed.

(1125) **Alloys of Silver.**—Various alloys of silver may be obtained with facility, but the only one extensively used is the alloy of silver with copper. Pure silver is too soft for ordinary uses, such as the fabrication of coin, and jeweller's work, and would soon waste by the constant friction it would experience. In order to confer a sufficient degree of hardness upon the silver, it is combined with a small quantity of copper. The proportion of copper in the 'standard' silver employed for coinage varies in different countries: in England it amounts to 7·5 per cent., in France to 10 per cent., and in Prussia to 25 per cent. English standard silver has a density of 10·30.

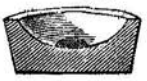
Experience has shown that an alloy of silver and copper, however carefully the two metals be incorporated, undergoes a species of liquation during the slow solidification of the melted mass; when cast into ingots, the interior parts of the bars have a composition different from that of the superficial portions,—a circumstance of some importance in the preparation of standard silver for the purposes of coinage. The only alloy in which this partial separation of the two metals was found not to occur is stated by Levol (*Ann. Chim. Phys.*, 1852, [3], xxxvi. 220), to consist of 719 parts of silver and 281 of copper, corresponding to the formula, Ag_8Cu_2; but even this, when allowed to cool very slowly, ceases to be homogeneous; its density is 9·9045. This liquation is comparatively trifling in amount in bars which contain 950 parts of silver and upwards in 1000: in bars, however, which contain a larger proportion of silver than 719 in 1000 of alloy, the central portions of the ingot were found to be richer than those upon the surface, and in the alloys of lower value the proportion of silver was greatest on the surface of the ingot.

Silver, when alloyed with many of the metals in small quantity, is rendered brittle and unfit for the purposes of coinage. This is the case, for instance, when the silver contains tin, zinc, antimony, bismuth, lead, or arsenicum. These metals are, however, easily removed in the ordinary course of refining. The alloy used as a *solder* for silver consists of 6 parts of brass, 5 of silver, and 2 of zinc. Silver appears to have the power of dissolving its sulphide; a quantity of sulphide not exceeding 1 per cent. renders the mass so brittle that it cannot be rolled, and a similar effect is produced by the presence of argentic selenide.

(1126) **Assay of Silver by Cupellation.**—From the high price of silver, compared with that of the metals used to harden it, it has become an object of great importance to be able to determine with

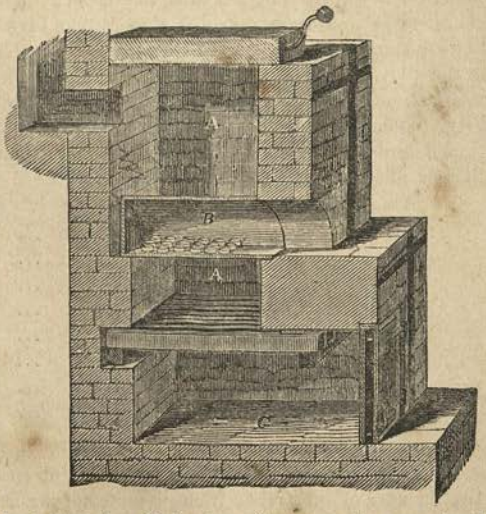
facility and accuracy the proportion of silver in any compound. Jeweller's silver must according to law be of a certain degree of fineness. In this country each article, previously to being sold, is tested at Goldsmiths' Hall, and if approved is stamped. The method of testing commonly employed is termed *assaying* or *cupellation.* In principle it depends upon the property possessed by lead of absorbing oxygen at a high temperature, and of forming with it an easily fusible oxide, which imparts oxygen with facility to all those metals which yield oxides not reducible by heat alone. Most of the oxides* thus formed unite with plumbic oxide, and produce a fusible glass which is easily absorbed by a porous crucible made of burnt bones, termed a *cupel;* whilst any silver that the mixture contains is left behind in a bright globule, which admits of being accurately weighed. The cupel and its contents are shown in section in fig. 367. These cupels are prepared from bone ash (burnt to whiteness, and ground to a fine powder), moistened with water: a suitable quantity of the mixture is placed in a mould, and the required form and coherence are given to it by the blow of a mallet or of a press: the cupels are allowed to dry thoroughly before they are used. The assay may be conducted upon 1 gram of silver.

Fig. 367.



The plan of proceeding is as follows:—In a convenient furnace, such as is shown in section at A A, fig. 368, is placed an earthenware oven or muffle, B, of semi-cylindrical form, closed at one end, and open at the other, with slits in the sides to allow the free passage of the air through the muffle: upon the floor of the muffle, a number of cupels are arranged in rows, and the temperature is raised to bright redness. Equal portions of the various samples of silver to be assayed are in the meantime accurately weighed, and wrapped in a quantity of pure thin sheet lead, the weight of which varies with the purity of the alloy; the larger the proportion of foreign metals that it contains, the greater is the quantity of lead needed. Each piece for assay is now placed

Fig. 368.



* Oxides of tin, zinc, nickel, and iron, do not form a fusible combination

in its allotted cupel, by means of a long pair of tongs. It fuses quickly; fumes of plumbic oxide are seen rising from the cupels, but the greater part of the oxide is absorbed by the cupel, and the silver is left behind in a state of purity. At the moment that the last portion of lead undergoes oxidation, the surface of the silver flashes, or lightens as it is technically termed, owing to the cause already explained (1059). This phenomenon indicates that the process is completed. The button is allowed to cool very gradually, to prevent the loss of silver by dispersion from *spitting* (1119); it is then detached from the cupel, brushed and accurately weighed. If the piece of alloy originally taken weighed 1 gram, the weight of the button in milligrams gives the number of parts of silver in 1000 parts of alloy. A minute quantity of silver always passes into the cupel during the process, for which an allowance must be made in weighing the button; and if the proportion of lead be too great this loss is increased, but if too little be used, part of the copper is left in the bead. Upon an alloy which contains 925 parts of silver to 75 of copper, the loss is about 4 per 1000; and upon silver which contains 900 parts in 1000, the loss on the button is about 5 parts in 1000, but the amount of this loss varies with the temperature. In order to be able to estimate the amount of this loss in each operation, the best plan is to pass three or four *proofs* with each set of assays. These proofs consist of pieces of fine silver of known weight, which are mixed with quantities of lead and copper, approximatively of the same amount as those present in the assays under trial. The loss experienced by these proofs affords a method of checking the results of the assay.

The most convenient system of reporting the fineness of silver is the decimal method, which is employed in most countries with the exception of England. The practice of reporting both gold and silver decimally was, however, introduced some years ago by Sir J. Herschel into the Mint of this country, and it probably will gradually supersede the cumbrous and artificial method which is still generally employed by the English assayers. Upon the decimal system, fine silver is termed 1000·0, and the report upon any sample of alloy simply indicates the number of parts of pure silver in 1000 which it contains. Thus English standard silver contains 925 parts of silver, and 75 of copper in 1000 of the alloy. French standard contains 900 parts of silver, and 100 of copper in 1000 of alloy. English standard would therefore be reported as 925; French standard as 900.

The proportions of lead which are generally employed for the cupellation of different alloys are the following:—

If 1000 parts of the alloy contain		It will require of lead
1000 parts of fine silver	... ...	half its weight.
950 „	... ...	3 times its weight.
925 „	... ...	5½ „
900 „	... ...	7 „
850 „	... ...	9 „
800 „	... ...	10 „
700 „	... ...	12 „
600 „	... ...	14 „
500, or less „	... ...	16 or 17 „

A skilful assayer will generally be able at once to determine the comparative fineness of an article from its mere appearance, and will judge accordingly

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with litharge, and the alloys which these metals yield with silver are consequently not adapted for cupellation.

of the proportion of lead which it will require. Great care is needful in regulating the temperature of the furnace during the cupellation; if too high, a part of the silver will be lost by volatilization; if too low, portions of lead and copper are liable to be retained. When the assay is properly performed, the button is brilliant, well rounded, free from irregularities, and somewhat granular upon its surface: it is readily detached from the cupel. If the assay adheres strongly to the cupel, or is irregular in its outline, it retains a portion of the alloy.

(1127) **Assay of Silver by the Wet Process.**—The results of the process of the assay by cupellation, even in experienced hands, may vary as much as 2 parts in 1000: this circumstance induced Gay-Lussac to contrive a different method, which is now adopted not only in the French Mint, but is employed in the Mints of Great Britain and the United States, as well as in almost all the Mints of Europe: it admits of an accurate estimate of the value of an alloy to within 0·5 in 1000. This process depends upon the solution of the alloy in nitric acid, the precipitation of the silver from the nitrate in the form of an insoluble chloride, and the measurement of the amount of a standard solution of sodic chloride which is required to effect the complete precipitation of the silver in a given weight of the alloy. Argentic chloride easily collects into dense flocks by agitation in a solution which is acidulated with nitric acid, and which contains no excess of soluble chlorides: so that the exact point at which the precipitate ceases to be formed is readily perceived.

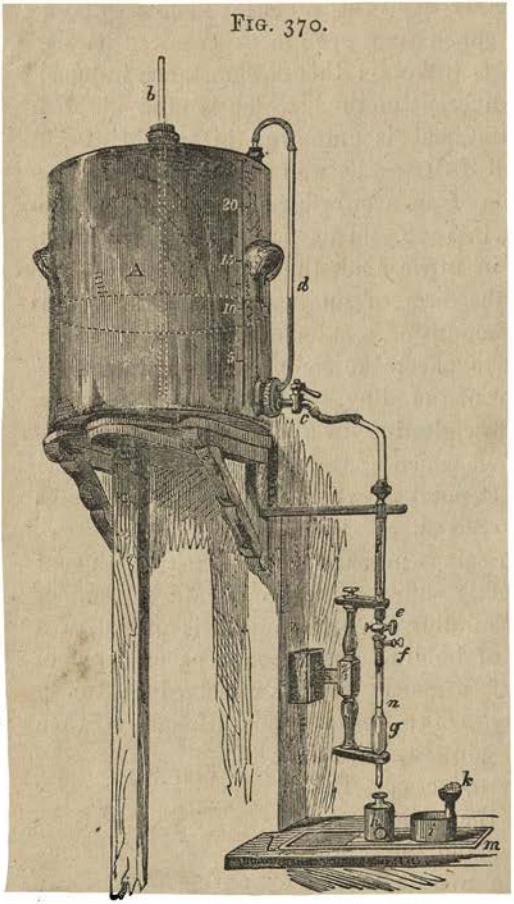
A solution of common salt is prepared of such a strength that 100 grams of it are exactly sufficient to precipitate 1 gram of pure silver. 1 gram of the alloy for examination is placed in a stoppered bottle capable of holding about 200 c. c., or 7 oz. of water, and by the aid of a gentle heat, is dissolved in 8 c. c. of nitric acid of density 1·25: the solution of salt is then placed in a burette (fig. 369) capable of holding rather more than 100 c. c. The burette, when filled with the solution, is weighed before being used, and the liquid is added to the argentic nitrate in the bottle; when it is supposed that the silver is nearly all precipitated, the liquor is briskly agitated in the bottle, and the precipitate is allowed to subside; a drop or two more of the solution of salt is then added: if a precipitate be produced, the liquid is again agitated, and when clear, more of the solution is added, as before, so long as any turbidity is produced by the addition. When a cloud ceases to be formed, the proportion of

FIG. 369.

solution of salt which has been added is ascertained by weighing the burette a second time. The number of decigrams of the solution employed indicates the degree of fineness of the alloy in thousandths.*

When, as in the assay of bars for coin or for jeweller's work, a large number of assays must be executed, all very nearly of uniform fineness, the operation may be reduced to a system by which its precision may be increased, at the same time that it is rendered much more easy of execution. For this purpose, two solutions of salt are employed: one, the *standard solution*, containing in 100 c. c. a sufficient quantity of commercial sodic chloride to precipitate 1 gram of silver;† the second solution, the *decimal solution*, having one-tenth of the strength of the first, and being prepared by diluting 1 litre of the standard solution with 9 litres of water. These solutions are to be preserved in well-closed bottles. The standard solution is prepared in large quantities at a time, and kept in a glass carboy, or in a stoneware jar, A, fig. 370, capable of containing from 90 to 125 litres (20 or 25 gallons): *b* is a tube open at both ends, which passes nearly to the bottom of the jar, to admit air, whilst the liquid is drawn off by the stopcock, *c*, without allowing any loss by evaporation; *d* is a gauge by which the quantity of liquid within is indicated. Several bottles, capable of containing about 200 c. c. (7 ounces) each, are fitted with ground stoppers, numbered consecutively from 1 upwards: into

FIG. 370.

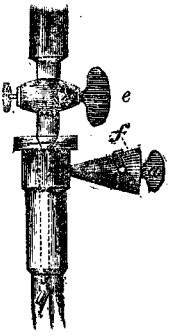


* In the Calcutta Mint this precipitate is washed by subsidence in the vessel in which it is formed, and is then collected in a small porcelain crucible, as in the process of collecting gold in the operation of *parting* (1155). The chloride is dried, and then weighed, and the corresponding value of the silver is calculated.

† This solution contains approximatively 5·416 grams of sodic chloride per litre; but as the commercial salt contains magnesic chloride, the exact strength

each bottle 1 gram of the alloy for assay is weighed; 8 c. c. of nitric acid are added to each bottle, which is placed in a shallow vessel containing water, and gradually raised to the boiling-point; in ten minutes the alloy is completely dissolved.

FIG. 371.



The precipitation of the silver in the form of chloride is then effected by the aid of the apparatus now to be described —*g*, fig. 370, is a glass pipette which can be filled with the standard solution. The quantity of liquid introduced into the pipette is regulated by means of the stopcock, *e f*, the peculiar construction of which is shown on a larger scale in fig. 371, in which *e* represents an ordinary stopcock (constructed of silver to resist the action of the solution), terminating below in a long tube, *c*; at *f* is an opening for the escape of air, which can be closed at pleasure by the plug, *a*. Suppose it be desired to fill the pipette, *g*, fig. 370; the lower opening of the pipette is closed by the forefinger, the solution is admitted by opening the stopcock, *e*, whilst the air escapes at *f*, which is open; as soon as the liquid has risen a little above the mark, *n*, both the stopcock, *e*, and the plug at *f*, are closed, and the finger is withdrawn. In this position the pipette will retain its charge for an indefinite time. The apparatus represented at *m l* is intended to facilitate the exact emptying of the pipette; the tray, *h i*, slides easily between two grooves, in which its motion is limited by the stops *l* and *m*; *h* is a compartment for the reception of the assay bottle, so adjusted that when the tray rests against the stop *m*, the pipette shall empty itself into the bottle without wetting its neck; *i* is another compartment for receiving the superfluous solution of salt, and *k* represents a piece of sponge, the object of which is to remove the drop which hangs to the lower end of the pipette; the stop *l* is so placed, that when the slide rests against it, the sponge shall just touch the lower extremity of the pipette. The sponge, *k*, having been brought to touch the lower end of the pipette, the plug at *f* is slightly relaxed to allow the air to enter, and a portion of the liquid gradually to escape, until it has fallen exactly to the mark *n*. The plug is now pressed firmly into its place, and the slide is moved until the bottle, *h*, is directly underneath the pipette; on opening the plug at *f* to its full extent, the charge flows freely into the bottle.

Suppose the object of the assay to be to ascertain whether a certain number of bars be of the fineness of English standard silver, or if not, what is the amount of their variation from that standard. The pipette, *g*, is so graduated that when filled up to the mark *n*, it shall deliver exactly 92·2 c. c. of the standard solution, which will contain a sufficient amount of common salt to precipitate 0·922 gram of silver; a quantity which is purposely rather less than the assay is expected to contain; 1 gram of alloy, if of correct composition, containing 0·925 gram of silver. When each bottle in succession has received from the pipette a charge of exactly the same value, they should be briskly shaken by hand until the argentic chloride has coagulated and settles quickly, leaving the supernatant liquid quite clear, or they may be transferred to the *agitator*, shown at fig. 372, which is suspended from an iron arm, *d*, between two strong springs, *e*, *e*, made of vulcanized caoutchouc. This agitator is usually constructed to contain 10 bottles, which are lodged in the compartments,

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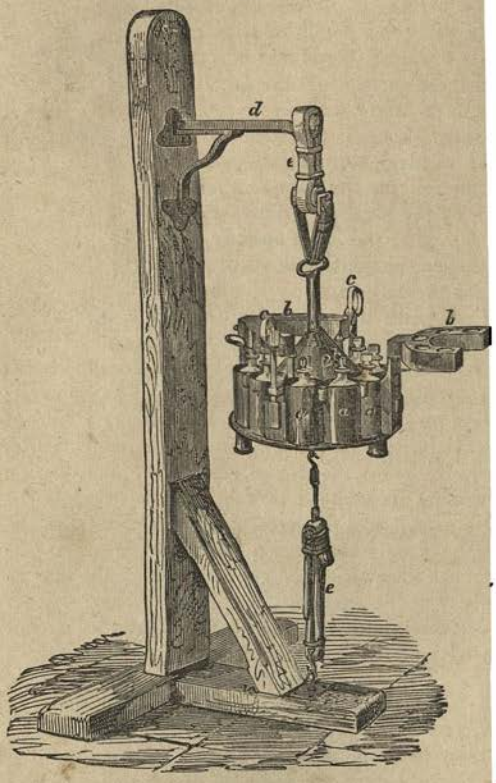
must be determined by dissolving a gram of fine silver in acid, and precipitating it by the addition of 100 c. c. of the solution, ascertaining the amount of the excess or deficiency of chloride in the manner about to be detailed, and then adding water or salt as may be needed.

a, *a*; the stoppers are secured in their places by the rims, *b*, *b*, one of which is represented in the figure as thrown back for the admission of the bottles; the rims when closed are confined by the springs shown at *c*, *c*. On agitating the apparatus briskly for 60 or 80 seconds, the solutions become clear, and the bottles are removed from the agitator, and transferred to a stand, behind which is a black board divided into 10 numbered compartments, each bottle being placed opposite the compartment which corresponds with its number: if the solutions in any of the bottles be not quite clear, they may be agitated for a few moments longer by hand.

FIG. 372.



The adjustment of the remaining portion of the assay is made by means of the *decimal solution*. This is contained in a small bottle of from 284 to 340 c. c. (10 or 12 ounces) in capacity, fig. 373, provided with a tube or small pipette, *b*, open at both ends, but drawn out to a narrow aperture below. On this small pipette a mark, *c*, is made at a height corresponding exactly to 1 c. c. of the liquid, 1 c. c. of this solution containing sufficient chlorine to precipitate 1 milligram of silver.

The assayer now plunges this small pipette into the decimal solution, and closing the upper opening of the tube with his forefinger, partially withdraws it from the bottle, and allows the liquid to escape until it stands exactly at the line of the graduation, *c*; he then transfers the pipette to the first bottle, and allows the solution to flow into it. The same operation is repeated with each assay bottle in succession. A mark is next made with a piece of chalk, opposite to each bottle in which a precipitate is occasioned. These bottles are then shaken a second time; the solutions having thus again been rendered clear, are replaced upon the table, and a second pipette of the decimal solution is added to each of the bottles in which a precipitate was first produced. This operation is repeated until in each bottle no further precipitate is occasioned. The contents of the pipette, *g*, of the standard solution which have been added to each assay, occasion a precipitate out of

FIG. 373.

the 1 gram equal to 0·922, or of 922 parts out of 1000 parts of alloy. Each pipette of decimal solution is equivalent to $\frac{1}{1000}$ of fine silver in the alloy, and by counting the number of marks against each bottle, the assayer ascertains the value of each bar. If, for instance, two marks stand opposite to any bottle, the fineness of the bar will be more than 923, but less than 924, and may be reported as 923·5: as, however, the decimal solution floats on the surface of the liquid and produces an opalescent cloud, the thickness of which varies with the quantity of silver still remaining in solution, it is possible for a skilful assayer to judge easily to $\frac{1}{4000}$ or ·25 of the silver in the alloy.

But suppose that there be some bottles in which the addition of the first pipette of the decimal solution produces no precipitate; these samples must be either exactly of the fineness 922, or below that point. The following method is adopted for completing the assay of these samples: a *decimal solution of silver* is prepared by dissolving 1 gram of pure silver in nitric acid, and diluting it with distilled water until the solution occupies the bulk of 1000 c. c. of water; each cub. centim. of this liquid will then contain exactly 1 milligram of silver. A bottle of this solution is provided with a pipette similar to that shown in fig. 373, but graduated to deliver 5 c. c. of the liquid from the mark *d*. Each of the assay bottles, which indicates a fineness below 922, is supplied with 5 c. c. of this decimal silver solution, or with 5 milligrams of silver; a mark − 5 is made upon the board against each of these bottles. The bottles are then agitated as before, and a fresh dose of 1 c. c. of the decimal *salt* solution is now added to each: if a cloud be thus produced, a mark is chalked against each bottle in which a precipitate is observed, and the bottles are again agitated, and another dose of decimal salt solution is added, and so on, until a precipitate ceases to be formed. Suppose that the first two pipettes of the solution produce a cloud, but the third does not; each bottle, it will be remembered, received a dose of salt solution in the first instance, as usual, in addition to the quantity received after the decimal silver solution was added; the quantity of salt which has produced a precipitate is therefore equivalent to 922 + 1 + 1½, or 924·5; but since 5 of silver has also been added beyond that which the alloy originally contained, the amount to be reported becomes 924·5—5, or the fineness of the bar is 919·5. It is preferable, in cases where the bars are below the standard, to add an excess of silver solution at once, and then to estimate the excess of silver in the manner above described; because if, instead of acting thus, successive doses of 1 milligram of silver be added until no further precipitate is formed, it becomes very difficult to render the solution clear by agitation.

The standard solution of salt is prepared at a temperature, say, of 15° (59° F.), consequently the pipette, *g*, will only deliver a volume of liquid rigorously equal to 922 milligrams of silver, at that temperature. At a higher temperature the liquid will expand, and a given volume will, therefore, contain a smaller amount of sodic chloride, whilst at a lower temperature it will contract, and will contain a larger amount. A correction for this variation in the strength of the liquid is, therefore, required. This is made very simply in the following manner:—Each time that a number of assays is made, a piece of fine silver, equal to ·925 gram, is weighed off, dissolved in nitric acid, and assayed as above directed. The number of pipettes of the decimal solution of salt which is required to complete the precipitation is noted, and the value of the contents of the large pipette of standard solution, *g*, is thus verified upon each occasion. If, for example, 2½ pipettes of decimal solution were required for completing this precipitation, the large pipette would deliver a quantity of the solution sufficient to precipitate 922·5 milligrams on that day, instead of 922. Any deviation from the calculated value is allowed for, and a correction is made upon the assays by means of a table constructed for the purpose.

It is easy to employ this solution for the assay of silver of other degrees of fineness; but it is necessary to know approximatively the value of the alloy, in order that a suitable weight of it may be dissolved in nitric acid. Suppose, for instance, a number of bars approximatively of the value of 900 (the French standard) are to be assayed: a piece of the alloy, which contains approximatively ·925 gram of fine silver must be taken; the quantity required is easily calculated, since the weight of the alloy needed will be inversely as its fineness; for 900 : 925 :: 1 gram : 1·0277 gram. The weight required in this case will consequently be 1·0277 gram.

Mercury is the only metal the presence of which interferes with the accuracy of the assay by the humid method; but the process may be modified so as to give correct results even in this case.

(1128) **Preparation of Fine Silver.**—In order that the foregoing process shall be accurately performed, it is necessary to be provided with silver of absolute purity. The following is one of the best methods of obtaining the metal in this condition. Standard silver is dissolved in nitric acid: the liquid is diluted, and decanted or filtered from undissolved particles of gold or of argentic sulphide, and the solution is precipitated by the addition of a solution of sodic chloride in slight excess. The precipitate is washed in a large jar by subsidence, until the washings are tasteless. The chloride is then mixed with oil of vitriol, in the proportion of 200 grams to each kilog. of chloride, and several bars of zinc are placed in the mass; the zinc speedily becomes converted into zincic chloride, which is dissolved, whilst the silver is reduced to the metallic state, and by a voltaic action the reduction gradually extends through the mass; $Zn + 2AgCl = Ag_2 + ZnCl_2$. The mixture is not to be agitated. In the course of a day or two the decomposition is usually completed. If a portion of the reduced silver, after being thoroughly washed, is entirely soluble in nitric acid, the reduction is complete. The bars of zinc, with the crust which adheres to them, are then carefully removed, and the reduced metal is digested for two days with dilute sulphuric acid, to remove any basic salt of zinc which may have been formed. The reduced silver, after being washed in a large vessel by subsidence until the washings cease to precipitate argentic nitrate, is dried and cast into ingots if desired. The metal is refined in large quantities for commercial purposes in this manner. It is not absolutely pure, and therefore, for delicate chemical operations, it undergoes a further process of purification.

For this purpose it is redissolved in nitric acid, and a second time precipitated as chloride, pure hydrochloric acid being employed as the precipitant: the precipitated chloride is again washed by subsidence until the washings no longer redden litmus. The chloride of silver is next dried until it ceases to lose weight, 100 parts of the chloride are mixed with 70·4 of chalk, and 4·2 of powdered

charcoal, and the mixture is heated in a deep clay crucible. The temperature is kept at a dull red heat for half an hour, after which it is gradually raised to full redness: a considerable disengagement of gas takes place, owing to the evolution of carbonic anhydride and carbonic oxide, and calcic oxychloride is formed, constituting a fusible slag, beneath which the pure silver collects; $2AgCl + 2CaCO_3 + C = Ag_2 + CO + 2CO_2 + CaO.CaCl_2$*. The silver may be poured into an ingot mould, re-melted in order to free it from slag, and afterwards rolled into sheets. Silver sufficiently pure for all ordinary purposes may also be obtained in a crystalline form by boiling a slightly acid solution of nitrate or other salt of silver with sheet copper: the precipitated silver is well washed, digested in a solution of ammonia, to remove any traces of adhering cupric oxide, and again washed. Perfectly pure silver is readily obtained by dissolving the silver in nitric acid, evaporating to dryness, and fusing the argentic nitrate; it is then redissolved, excess of ammonia added, and the clear solution decomposed by heating it at about 70° (158° F.), with a slight excess of ammoniacal cuprous sulphite, or by a mixture of ammonic sulphite with an ammoniacal cupric salt: the precipitated silver, after being digested with concentrated aqueous ammonia, is washed and dried (Stas). Pure silver may also be obtained by reducing an ammoniacal solution of argentic chloride with zinc, and subsequently treating the reduced metal first with strong hydrochloric acid and then with ammonia.

(1129) **CHLORIDES OF SILVER.**—There are two chlorides of silver, the subchloride, (?)Ag_4Cl_3, and the protochloride, AgCl.

Argentous Chloride, or *Subchloride of silver*, Ag_4Cl_3, is usually directed to be prepared by digesting leaves of pure silver in a solution of cupric chloride or of ferric chloride; it may also be prepared by the long-continued action of hydrochloric acid on argentous citrate, prepared by reducing the argentic salt with hydrogen. It forms black scales or a black powder; it is not acted upon by nitric acid, but is resolved by ammonia into argentic chloride and metallic silver. Potassic hydrate and acetic acid have no action on it.

(1130) **ARGENTIC CHLORIDE,** or *Chloride of silver*; AgCl = 143·5; *Density*, 5·552; *Comp. in* 100 *parts*, Ag, 75·26; Cl, 24·74.—This compound is found native, either crystallized in cubes, or as a compact semi-transparent mass, known by the name of *horn silver*. It is procured as a dense white flocculent precipitate on adding hydrochloric acid or the solution of any chloride to a solution of a salt of silver: when moist it quickly assumes a dark violet colour on exposure to the sun's light, and a similar change is produced gradually by diffused daylight: it also becomes darkened when heated, in the dry state, above 100° (212° F.), even in the dark. Chlorine is set free under these circumstances, and the subchloride appears to be formed. If the chloride be moistened with a solution of argentic nitrate and exposed to the sun in a thin layer, a strong odour of hypochlorous acid is immediately developed.

Argentic chloride is insoluble in pure water, and in all the

* The washed chloride may also be reduced without difficulty by fusion with about half its weight of dried sodic carbonate.

dilute acids. A solution of silver containing not more than 1 part of the metal in 200,000 of water is immediately rendered opalescent by the addition of hydrochloric acid. Argentic chloride is, however, taken up by boiling hydrochloric acid, and by strong solutions of the chlorides of metals of the alkalies and alkaline earths, with which it forms crystallizable double salts; they are decomposed if their solutions are diluted; advantage is taken of this circumstance in the extraction of silver (p. 837). Argentic chloride is decomposed by digestion with a solution of potassic bromide or iodide, argentic bromide or iodide being produced, whilst potassic chloride remains in the solution. Field, by whom this result was observed (*Jour. Chem. Soc.*, 1857, x. 236), has proposed to employ it for determining the proportions of chlorine, bromine, and iodine in the analysis of a mixture in which they occur together.

Argentic chloride melts at about 260° (500° F.), and when very strongly heated it is partially volatilized; on cooling it forms a horny, semi-transparent, sectile mass. It is not decomposed by ignition with carbon, but is easily reduced when heated in a current of hydrogen, hydrochloric acid being formed, whilst metallic silver is set free. Zinc, iron, and many of the easily oxidizable metals, also reduce moist argentic chloride: this reaction is turned to account in the refining of silver on the large scale (1128). It is not necessary that the argentic chloride be freshly precipitated, although, if it be, the operation is more rapid; a cake of the fused chloride laid upon zinc or iron, and covered with acidulated water, will after some days be completely reduced to a spongy mass of metallic silver.

Weak alkaline leys do not act upon argentic chloride, but if it be boiled with a concentrated solution of potassic hydrate, potassic chloride is formed, and a dense, black, argentic oxide is produced; the addition of glucose to this mixture rapidly reduces the oxide to the state of metallic silver. A solution of ammonia dissolves the chloride freely, and deposits it again, by evaporation at ordinary temperatures, in transparent, colourless crystals; if the solution be boiled with potassic hydrate, fulminating silver is deposited. The ammoniacal solution also readily furnishes metallic silver if it is poured very slowly into a boiling solution of 5 parts of grape-sugar, and 15 of crystallized sodic carbonate in 200 of water for every 4 parts of argentic chloride. If the liquid be kept boiling during the whole time, the silver is deposited in the form of a yellowish grey powder which is easily washed. The solid chloride absorbs ammoniacal gas rapidly, but

it is given off again when the compound is heated (391). When argentic chloride is ignited with the carbonates of the alkali-metals, chlorides of these metals are formed, and pure silver is left; this reaction furnishes a means of obtaining large quantities of silver in a state of purity; $4AgCl + 2Na_2CO_3 = 2Ag_2 + 4NaCl + 2CO_2 + O_2$. Argentic chloride dissolves in boiling concentrated sulphuric acid with evolution of hydrochloric acid and formation of argentic sulphate. It also appears to be decomposed by the long-continued action of boiling nitric acid; for when the latter is distilled from finely-divided argentic chloride, argentic nitrate is found in the retort. Argentic chloride is soluble in solutions of the thiosulphates (hyposulphites), forming compounds of an intensely sweet taste: by evaporating these solutions crystalline double thiosulphates (hyposulphites) may be obtained (433). Potassic cyanide likewise dissolves argentic chloride, forming potassic chloride and argentic potassic cyanide, KCy.AgCy. The soluble sulphites, and ferric chloride also dissolve argentic chloride.

(1131) **ARGENTIC BROMIDE**, or *Bromide of silver;* AgBr = 188; *Density*, 6·353; *Comp. in* 100 *parts*, Ag, 57·45; Br, 42·55.—This constitutes a rare mineral which has been found in Chili; but it occurs in tolerable abundance at the mine of Chañarcillo, in Atacama, mixed with variable proportions of argentic chloride. The bromide may be formed artificially by adding a solution of potassic bromide to one of argentic nitrate. It is of a yellowish colour, is insoluble in water, and much less soluble in ammonia than the chloride. Acids do not dissolve it, but it is decomposed by chlorine, bromine being liberated and argentic chloride produced. Argentic bromide fuses below a red heat. It is soluble in a concentrated solution of potassic bromide, and in other bromides, forming double salts, which are decomposed by dilution with water. Argentic bromide is soluble in a solution of sodic thiosulphate (hyposulphite of soda).

(1132) **ARGENTIC IODIDE**, or *Iodide of silver;* AgI = 235; *Density at* 116° (240°·8 F.), 5·816 (Rodwell); *Comp. in* 100 *parts*, Ag, 45·96; I, 54·04.—This compound is found in Mexico, mixed with calcic carbonate, native silver, and plumbic sulphide. It may be prepared artificially by adding a solution of potassic iodide to one of argentic nitrate; it then forms a pale yellow, flocculent precipitate, which is scarcely acted on by light unless metallic silver or argentic nitrate be present: it is insoluble in acids, and almost so in ammonia. It may also be obtained by acting upon metallic silver with hydriodic acid, which dissolves

the metal with evolution of hydrogen, and gradually deposits six-sided prisms of the iodide. Argentic chloride is also rapidly converted into the iodide when treated with hydriodic acid. It fuses easily into a dark orange-yellow mass, which becomes bright yellow and opaque, on cooling. It is decomposed by zinc in the presence of moisture. Chlorine displaces the iodine from the salt. Argentic iodide is soluble in a hot solution of hydriodic acid, which on cooling deposits flaky crystals of a compound of the acid with argentic iodide, having the composition, AgI.HI. The iodide is likewise soluble in concentrated solutions of potassic iodide, as well as in those of sodic thiosulphate (hyposulphite of soda).

(1133) **ARGENTIC FLUORIDE**, or *Fluoride of silver*, AgF= 127, is freely soluble in water; it is obtained by dissolving argentic oxide or carbonate in dilute hydrofluoric acid and evaporating in a platinum dish, but it generally contains a little metallic silver. It differs remarkably from the other haloid compounds of silver in being deliquescent and very soluble in water. A hydrated salt may be obtained in crystals.

(1134) **OXIDES OF SILVER.**—Silver forms three oxides; a suboxide, Ag_4O; argentic oxide, Ag_2O, which is the basis of the salts of the metal; and a peroxide, probably Ag_2O_2, which does not combine with acids.

(1135) **ARGENTOUS OXIDE**, or *Suboxide of silver*, Ag_4O.—According to Wöhler, if argentic citrate be heated at 100° (212° F.), in a current of hydrogen, the salt loses half an equivalent of oxygen, and a compound is produced which is sparingly soluble in water, forming a brown solution, from which, on the addition of potassic hydrate, a suboxide of silver is precipitated: it also appears to be produced by the action of hydric peroxide on metallic silver. This compound is very unstable; hydrochloric acid converts it partially into subchloride, but it is decomposed by other acids, and by ammonia, into argentic oxide and metallic silver. A mixture of metallic silver and argentous oxide is also obtained by boiling the yellow triargentic arsenite with a strong solution of sodic hydrate, trisodic arsenate being simultaneously formed, $2Ag_3AsO_3 + 6NaHO = Ag_4O + Ag_2 + 2Na_3AsO_4 + 3H_2O$.

(1136) **ARGENTIC OXIDE**, or *Protoxide of silver*; Ag_2O= 232; *Density*, 7·2; *Comp. in* 100 *parts*, Ag, 93·1; O, 6·9.—This oxide may be obtained by boiling argentic chloride with a concentrated solution of potassic hydrate or by adding a solution of potassic or sodic hydrate to a solution of the nitrate or any other soluble salt of silver. A brown hydrated oxide falls, which readily parts with its water, and if dried at a temperature above 60° (140° F.), becomes anhydrous; it gives off oxygen below a red heat, and is reduced to the metallic state. Light also reduces it, and hydrogen, even at 100° (212° F.), has a similar effect;

contact under water with metallic tin or copper also deprives it of oxygen. Argentic oxide is a powerful base, easily acted upon by acids, yielding salts which in some cases are isomorphous with the corresponding salts of sodium. They are almost always anhydrous. By the action of nitric acid it produces a salt which does not redden litmus. Argentic oxide is slightly soluble in pure water, to which it communicates a feebly alkaline reaction. It combines with the fusible silicates, and is sometimes employed for producing a yellow glass.

(1137) **ARGENTIC PEROXIDE**; Ag_2O_2?; *Density*, 5·474.—This compound is obtained in dark grey, acicular crystals, when a concentrated solution of argentic nitrate is decomposed by means of the voltaic current. The peroxide accumulates upon the positive plate, but it always retains a certain quantity of undecomposed argentic nitrate. It is a conductor of the voltaic current. Acids decompose it, forming a salt of argentic oxide, whilst oxygen gas escapes. It is also decomposed with effervescence by ammonia, owing to escape of nitrogen.

(1138) **FULMINATING SILVER.**—Although potassic and sodic hydrates do not dissolve argentic oxide, it is freely soluble in ammonia, and the solution, by exposure to the air, deposits a black, micaceous powder, which is powerfully explosive, and which has received the name of fulminating silver. It is also produced if freshly precipitated argentic oxide be digested for some hours with a concentrated solution of ammonia; a black powder is formed which is allowed to dry in minute quantities on separate pieces of filtering paper. The same compound is formed on precipitating an ammoniacal solution of argentic nitrate or chloride by the addition of potassic hydrate, or when argentic peroxide is treated with ammonia, nitrogen being evolved. It is necessary to be aware of these facts, as it is a most dangerous substance, and might be produced unintentionally. Friction or pressure, even when under water, causes it to explode; and when dry, its detonation often occurs without any assignable cause. Acids immediately decompose it into an ammoniacal salt, and the corresponding salt of silver. The composition of this body, owing to its dangerous character, has not yet been accurately determined, but it is generally supposed to be a nitride, similar to that which is obtainable from mercury (1114).

(1139) **ARGENTIC SULPHIDE**, or *Sulphide of silver*; $Ag_2S = 248$; *Density*, 7·2; *Comp. in* 100 *parts*, Ag, 87·1; S, 12·9.—This compound is the principal ore of silver. It is found native, sometimes crystallized in cubes or octahedra, at other times massive. It has a leaden-grey metallic lustre, from which it derives its mineralogical name of *silver glance*. Argentic sulphide is isomorphous with cuprous sulphide, and sometimes displaces it in certain minerals, such, for example, as *polybasite*, and *fahlerz* or grey copper ore (1048).

Silver has a very powerful attraction for sulphur. The metal becomes tarnished, owing to the formation of a film of sulphide,

if it be exposed to the action of sulphuretted hydrogen in the gaseous state, even when largely diluted with air; and a black spot is immediately produced upon its surface by contact with a solution of a sulphide of one of the metals of the alkalies or alkaline earths. Argentic sulphide may be obtained as a black precipitate by passing a current of sulphuretted hydrogen through solutions of the salts of silver, or it may be prepared by heating silver with an excess of sulphur in a covered crucible; in this case the excess of sulphur is volatilized, and the argentic sulphide fuses, forming a dark grey crystalline mass as it cools.

Argentic sulphide is soft enough to allow of its being cut with a knife; it also possesses sufficient malleability to receive impressions from a die. According to Skey, it appears to conduct the voltaic current as readily when cold as when heated, and that without undergoing decomposition. It is easily fusible, and may be melted in closed vessels without change; if roasted in the air, however, the sulphur is gradually converted into sulphurous anhydride, and metallic silver is left: during this operation a portion of it is usually converted into argentic sulphate, which requires an elevated temperature for its decomposition.

Argentic sulphide is decomposed when boiled with concentrated sulphuric acid, sulphurous anhydride and argentic sulphate being formed. Strong nitric acid also dissolves it by the aid of heat.* Boiling hydrochloric acid converts it into argentic chloride, with evolution of sulphuretted hydrogen. Cupric chloride converts it into argentic chloride, with the formation of cuprous chloride and sulphide of copper: this change is much facilitated by the presence of sodic chloride in a moist state, as by its means both the argentic chloride and the cuprous chloride are dissolved at the moment of their formation. These reactions become important in the extraction of silver from its ores (1120). Argentic sulphide is also decomposed when heated with the alkalies, and a similar effect is produced by igniting it with iron, copper, lead, and many other metals.

Argentic sulphide dissolves in a solution of potassic cyanide, but it is not soluble in solutions of the alkaline sulphides: it unites with many other metallic sulphides, however, when fused with them. A native compound of this description is found in *red silver ore*, which is a double sulphide of silver and antimony,

* Argentic nitrate forms with the sulphide a yellow compound, $Ag_2S.AgNO_3$, insoluble in cold nitric acid, but decomposed when washed with boiling water. It is left in the form of a yellow powder when silver containing sulphide is dissolved in warm nitric acid of density 1·2.

$3Ag_2S.Sb_2S_3$, or Ag_3SbS_3 [$Sb(SAg)_3$]. In this mineral a portion of antimonious sulphide is often displaced by arsenious sulphide.

(1140) **Silver Ultramarine.**—When ultramarine is heated at 120° (248° F.), for some hours with a solution of argentic nitrate it becomes yellow, and is converted into a mixture of silver ultramarine and metallic silver: the latter can be removed by first converting it into argentic iodide by treatment with an alcoholic solution of iodine, and then dissolving it out by potassic iodide. The new compound, which is ultramarine in which the sodium is replaced by silver, is lemon-yellow. When treated with a small quantity of hydrochloric acid there is no action, but with a larger quantity it is decomposed with evolution of sulphuretted hydrogen. It is blackened by sodic hydrate or sulphide, but ultramarine is not regenerated.

(1141) **ARGENTIC SULPHATE,** or *Sulphate of silver;* $Ag_2SO_4=312$; *Density,* 5·322; *Comp. in* 100 *parts,* Ag_2O, 74·36; SO_3, 25·64.—When silver is boiled with sulphuric acid, a portion of the acid is decomposed and gives oxygen to the silver, which is converted into a sulphate, whilst sulphurous anhydride escapes: the sulphate is dissolved by the excess of acid, but is deposited in great part on the addition of water, of which it requires 88 times its weight for solution at 100° (212° F.), and 200 parts at the ordinary temperature. It may be obtained in small rhombic prisms, which are isomorphous with those of anhydrous sodic sulphate. They fuse readily; but they require a higher temperature for their decomposition than is needed to decompose the sulphates of iron or copper (p. 837). Small quantities of gold are separated from silver on the large scale, by boiling 1 part of the alloy, finely granulated, in cast-iron vessels with 2½ parts of oil of vitriol; the gold is left behind as a fine powder. The solution of silver is afterwards diluted until of a density of 1·200, introduced into leaden vessels, and the silver precipitated from the solution in the metallic form by bars of metallic copper. This process has been economically applied to the extraction of the gold contained in old silver coin, even where the proportion of gold did not exceed 1 part in 2000. It cannot be advantageously practised upon alloys containing more than about 200 parts of gold per 1000. If copper be present, its proportion should not exceed 4 per cent. of the mass; otherwise the cupric sulphate, owing to its sparing solubility in the acid, impedes the operation. An acid salt, *hydric argentic sulphate,* $AgHSO_4$, is obtained in pale yellow prisms on dissolving the normal salt in less than three parts of concentrated sulphuric acid. Crystallized argentic sulphate rapidly absorbs ammonia to the extent of 2 molecules for each molecule of the salt. A hot solution of

ammonia dissolves the salt freely, and on cooling deposits crystals composed of $4NH_3.Ag_2SO_4$.

Silver Alum, $Ag_2Al_24SO_4.24OH_2$, may, according to Church, be obtained in octahedral crystals by heating argentic sulphate and aluminic sulphate in equivalent proportions with a little water, until the silver salt has dissolved. An excess of water separates it into its component salts.

Argentic Sulphite is obtained as a white precipitate on adding a solution of sulphurous acid to one of argentic nitrate, taking care to avoid excess of the acid. It is readily decomposed by heat, yielding silver, argentic sulphate, and sulphurous anhydride.

(1142) **ARGENTIC NITRATE,** or *Nitrate of silver;* $AgNO_3 = 170$; *Density,* 4·336; *Comp. in* 100 *parts,* Ag_2O, 68·24; N_2O_5, 31·76, or Ag, 63·53.—This salt is readily formed by dissolving silver in moderately strong nitric acid. If standard silver be employed in its preparation, the cupric oxide is easily separated from the solution by boiling it with freshly precipitated argentic oxide, which may be obtained by precipitating a portion of the same solution by potassic hydrate, and washing the precipitate, the presence of cupric oxide being unimportant. It crystallizes in square, colourless, anhydrous tables, which require an equal weight of cold water for solution, but are almost insoluble in strong nitric acid. Boiling alcohol dissolves about a fourth of its weight of the salt, but deposits most of it on cooling. The nitrate fuses at 219° (426°·2 F.), and if then cast into cylindrical moulds, it forms the sticks of *lunar caustic* (from *luna,* the alchemical name for silver) employed by surgeons as an escharotic. By a more elevated temperature it is decomposed, argentic nitrite is produced, and at a still higher temperature metallic silver is left.

Argentic nitrate, when pure, undergoes no change by the action of light; but it is readily decomposed by the combined action of light and organic matter, which last it usually stains black. The stain thus produced cannot be removed by washing with soap and water; from this property it has been employed as the basis of an ink for marking linen, which may be prepared as follows:—Dissolve 10 grams of argentic nitrate and 5 grams of gum arabic in 35 c. c. of water, and colour the liquid with Indian ink. It is requisite to prepare the cloth first, by moistening the spot to be marked with a solution of sodic carbonate, which is allowed to become dry. This preparatory solution may consist of 80 grams of crystallized sodic carbonate, and 10 grams of gum, dissolved in 160 c. c. of water.* The black stains of

* A solution of coal-tar in naphtha forms a cheap indelible marking ink, which resists the action of chlorine, and is used by bleachers to mark their goods.

argentic nitrate may be removed from the hands or from linen by the employment of a strong solution of potassic iodide; potassic cyanide is still more effectual, but some danger attends its use. A solution of argentic nitrate is partly reduced, with deposition of metallic silver, when a current of pure hydrogen is passed through it for a long time. Dry argentic nitrate absorbs 3 molecules of ammonia, and if ammoniacal gas be passed into a concentrated solution of the salt, crystals of the *ammonio-nitrate* having the composition, $2NH_3.AgNO_3$, are deposited.

When metallic silver in fine powder is digested in a solution of argentic nitrate it is dissolved, and a yellow solution is formed analogous to that obtained when lead is similarly treated (1078).

(1143) **TRIARGENTIC PHOSPHATE**, or *Triphosphate of silver*, $Ag_3PO_4 = 419$; *density*, 7·321.—This salt is of a yellow colour, which is speedily changed by the action of light. It is very soluble in excess both of nitric acid and of ammonia. It is easily prepared by precipitating a solution of the ordinary hydric disodic phosphate by one of argentic nitrate; it fuses if heated above redness. *Argentic pyrophosphate* ($Ag_4P_2O_7$; *density*, 5·306), is obtained in like manner by precipitating argentic nitrate by sodic pyrophosphate; it is a white precipitate slowly darkened by light, and is easily fusible. The *metaphosphate*, $AgPO_3$, is obtained by precipitation from the argentic nitrate by solutions of sodic metaphosphate; it forms a gelatinous mass, which softens even at a heat of 100° (212° F.), and is soluble in excess of argentic nitrate. If boiling water be poured upon this precipitate, it fuses; acid is removed, and a submetaphosphate is left, consisting of $Ag_6P_4O_{13}$, or $4AgPO_3.Ag_2O$.

(1144) **ARGENTIC CARBONATE**; $Ag_2CO_3 = 276$.—This compound is readily obtained by precipitating a dilute solution of argentic nitrate with one of sodic or potassic carbonate. It is almost white when first precipitated, but when thoroughly washed acquires a yellow colour: it blackens when exposed to light. Heated at 200° (392° F.) it loses carbonic anhydride, and at a higher temperature oxygen is given off and metallic silver left.

Argentic carbonate is soluble in ammonia, and on adding alcohol to the solution a grey-coloured precipitate of *ammonio-argentic carbonate*, $Ag_2CO_3.4NH_3$, is produced.

(1145) **Characters of the Salts of Silver.**—The soluble salts of this metal are colourless, and most of them are anhydrous; they do not redden litmus; they have a powerfully acrid, metallic, astringent taste, and act as irritant poisons. *Before the blowpipe* they are readily reduced on charcoal to the metallic state, especially when mixed with sodic carbonate. In the oxidizing flame they give a yellowish bead with microcosmic salt. In solution, the salts of silver present the following reactions:

The *alkaline hydrates* give a brown hydrated oxide, insoluble in excess of the precipitant; *ammonia*, a brown precipitate, readily soluble in excess of ammonia; *potassic* and *sodic carbonates*, a white argentic carbonate, insoluble in excess, but soluble in

ammonic sesquicarbonate. *Sulphuretted hydrogen* and *ammonic hydric sulphide* give a black precipitate of argentic sulphide, not soluble in ammonia or in the sulphides of the alkali-metals. But the most characteristic test is the action of *hydrochloric acid*, or of a *soluble chloride*, which produces a white curdy precipitate of argentic chloride, insoluble in nitric acid even when boiling, but readily soluble in ammonia; it is also soluble in sodic thiosulphate (hyposulphite of soda), with which it forms an intensely sweet solution; potassic cyanide also dissolves it: argentic chloride speedily assumes a violet tinge when exposed to light; this change is retarded by the presence of free chlorine as well as by that of free nitric acid, and is prevented by the admixture of a small proportion of mercuric chloride. *Potassic iodide* or *bromide* gives a yellowish-white precipitate of argentic iodide or bromide, sparingly soluble in ammonia. *Hydrocyanic acid* and *potassic cyanide* give a white curdy precipitate of argentic cyanide, which is soluble in excess of potassic cyanide, easily soluble in ammonia, insoluble in dilute nitric acid, but soluble in boiling nitric acid if concentrated. *Phosphoric, chromic, oxalic, tartaric,* and *citric* acids, all form insoluble precipitates with salts of silver. Indeed, silver furnishes a greater number of insoluble salts than any other metal; they are almost all neutral in composition, and generally dazzling white. Most of them, however, become dark coloured when exposed to the action of light. Nearly all of them are soluble in ammonia, and many of them also in nitric acid. *Many metals* reduce solutions of the salts of silver, and throw down the silver from them in a metallic state, as is beautifully shown by the action of mercury, which produces a crystalline deposit consisting of an amalgam of silver, forming what has been termed the *arbor Dianæ*.* Copper and zinc also precipitate silver from its solutions. *Phosphorus* becomes coated with metallic silver if placed in a solution of any of its salts. A solution of *ferrous sulphate* also precipitates silver in the metallic form from its solutions, if they do not contain free nitric acid. If a solution of ammonia-nitrate of silver be added to one of ferrous sulphate, an intensely black precipitate ($Ag_4O.2FeO.Fe_2O_3$; H. Rose) is produced. This reaction is extremely sensitive for very small quantities of iron.

The compounds of silver exhibit a less strongly marked ten-

* On one occasion, the late Professor Miller found the long, thin, prismatic crystals to have the composition, Ag_2Hg_3, containing 26·45 per cent. of metallic silver.

dency to form double salts than is the case with the other noble metals.

(1146) **Estimation of Silver.**—Silver may be estimated either in the metallic state, as in the process of cupellation,—or in the form of chloride, 100 parts of which, after fusion, correspond to 75·26 of the metal. This precipitation is best effected by acidulating the liquid with nitric acid, and adding hydrochloric acid in slight excess. After the precipitate has been collected and dried, it should be detached from the filter, and fused in a porcelain capsule; on burning the filter, the portions of chloride retained by it are partially reduced to the metallic state by the hydrogen of the paper; the ash must therefore be moistened, first with nitric, and then with hydrochloric acid, to reconvert it into chloride, the excess of acid being afterwards expelled by heat.

(1147) **Separation of Silver from other Metals.**—This is readily effected by means of hydrochloric acid. If lead be present the solution must be diluted largely: should mercury be in solution, it must be converted into a mercuric salt by boiling the liquid with nitric acid, after which the silver may be precipitated in the form of chloride.

§ III. GOLD (Aurum): Au = 196·6.

(1148) **GOLD**: *Density*, 19·34;* *Fusing-pt.* 1037° (1899° F.); *Monad in Aurous salts, as* AuCl; *Triad in Auric salts, as* $AuCl_3$. —This valuable metal has been prized from the earliest ages of the world. It is found in small quantities in numerous localities, and always occurs in the native state, either crystallized in cubes, octahedra, or tetrahedra,—or in plates, in ramified masses, or in nodules or *nuggets*, which sometimes weigh many kilograms.† Native gold is always alloyed with silver; sometimes small quantities of osmium and iridium, copper, antimony, and in some rare instances, tellurium, are found accompanying it. No regular veins of gold are met with; it commonly occurs either in primitive or volcanic rocks, or in the alluvial deposits of certain rivers. Its most celebrated mines are those of California and Australia; and those of Mexico, Chili, Brazil, and Peru. In California the gold is chiefly found upon the Sacramento and its tributary streams, in deposits formed by the disintegration of quartz and

* Rolled gold, according to Rigg, has a density of 19·2982.

† A specimen of native gold, nearly free from earthy impurities, from the Kingower diggings, Australia, weighing 1743 oz., was exhibited in England in the early part of 1858, and still larger masses have been found since then.

granite. In Australia the gold is also associated with quartz, and occurs in slate rocks equivalent to the Cambrian formations of England and Wales, in the detritus of which the most productive gold-fields occur, in the deep gullies at the base of the rocky ranges of clay-slate, mica schist, and red and yellow sandstone. In this alluvium the gold is usually found at a depth of from 10 to 40 feet (3 to 12 metres), resting upon a 'bottom' of pipeclay. A good deal of gold is still obtained from the Ural Mountains; gold mines have also been worked in Wales, in the Cader Idris district. Many of the rivers of Africa likewise contain it among their sands, as do those of Hungary, Transylvania, and Piedmont: in these European countries it is principally extracted from the river sands by gipsies.

(1149) **Extraction of Gold.**—The operations for obtaining gold from its deposits differ from those required by almost every other metal, in being for the most part purely mechanical. According to Mr. Wathen (*The Golden Colony*, p. 71), the Australian digger formerly used a *cradle* for washing the ore, but this is not adapted to the stiff clays of the Australian gold-fields. The miner now, after having raised the 'washing stuff' from the pit, introduces it into the 'puddling tub,' which is merely one-half of a porter cask. The tub is half-filled with the washing stuff, water is baled in from the creek, and the whole worked about with the spade until the clay has become diffused through the water; this turbid water is poured off, and fresh water added, until, by repetition of the washing, 'nothing but clean gravel, sand, and gold remains. The gold is now readily separated from the gravel by means of a cradle, or simply by a tin dish. In the latter case, the dish is held half-immersed obliquely in water, and the gravel gradually washed away from the gold by the dexterous handling of the dish.'

The Californian 'Long Tom' consists of a trough about 16 inches (0·4 metre) wide, and 10 or 12 feet (3 or 4 metres) long, inclined so as to cause the water to run down rapidly: an iron grating, perforated with holes as large as a sixpence, forms the lower end, and is tilted in an opposite direction to the trough. Through the trough a current of water is kept constantly flowing. The auriferous earth is thrown in at the head, and as it is washed down by the stream, it is worked about with the spade, so that the earth and clay are quickly washed away; when the clean gravel reaches the lower end, it is arrested by the iron grating, and removed with a shovel, while the gold and sand fall through

into a box placed beneath. The contents of the box are again washed to extract the gold.

Auriferous quartz is first crushed, then stamped and ground to powder, from which the gold is subsequently extracted by amalgamation.

Much of the gold in circulation before the discovery of the deposits in Australia and California was obtained from auriferous pyrites. This mineral is coarsely pulverized either before or after roasting, and washed: the heavier particles of gold subside, and are extracted from this concentrated portion by amalgamation, the excess of mercury being separated by distillation.* Various methods are adopted for washing the auriferous material: in Mexico this operation is usually performed by negresses, who having pulverized the ore under flat stones, agitate it in wide, shallow, wooden dishes, separating the lighter portions with much dexterity. In Europe, the pyrites is ground and amalgamated, in mills constructed for the purpose. Those who wash the river sands usually select some spot at the bend of the stream, where the mud appears to be black or reddish; as it is here, if anywhere, that the gold is found. The most favourable time is when the waters are subsiding after storms or heavy rains: the sand is concentrated either by washing it in shallow vessels, or else by allowing it to pass through a succession of troughs. Amalgamation is afterwards resorted to, and the product is distilled, as in the analogous process for obtaining silver.

(1150) **Properties of Gold.**—Gold is of a rich yellow colour and high metallic lustre. It is not remarkable for its hardness, being, when in a pure state, nearly as soft as lead. Its ductility, however, is considerable, ranking next to silver, so that it may be drawn into very fine wire.

As already mentioned, it is the most malleable of the metals, and so extreme is the thinness to which it may be reduced by hammering, that 280,000 leaves placed upon one another would be required to occupy the thickness of one inch (or 11,200 in a millimetre). The thickness of the film may be still further reduced by floating it upon a dilute solution of potassic cyanide. Faraday found that such a film when attached to a plate of glass still retained its power of reflecting yellow light and transmitting green: if, however, the temperature were maintained for a short time at a point which need not exceed 315°·6 (600° F.), the metallic lustre disappeared entirely, and the transmitted light became of a pure ruby red, but the pressure of agate, or of any kind of hard body upon the film, changed the colour of the transmitted light at that spot to green (*Phil. Trans.*, 1857, 147).

Gold fuses at a temperature of 1037° (1899° F., Becquerel). It cannot be advantageously employed for castings, as it shrinks greatly at the moment of solidifying. It is but very slightly volatile in the heat of the furnace, although by a powerful electric

* Mr. Crookes has shown that the amalgamation is greatly facilitated by adding to the mercury a small proportion of an alloy of sodium and zinc. The sodium enables the mercury to wet the surface of the gold immediately, and diminishes the loss of both gold and mercury.

discharge, by the concentration of the sun's rays with a large convex lens, or by the intense heat of the oxyhydrogen jet, it may be dispersed in purple vapours. It is one of the most perfect conductors both of heat and of electricity. Gold suffers no change by exposure to air and moisture at any temperature. None of the simple acids, with the exception of selenic, has any effect upon it, but it is dissolved by any mixture which liberates chlorine. Its usual solvent is aqua regia, which for this purpose is generally prepared by mixing 1 part of nitric acid and 4 parts of hydrochloric acid. The alkaline hydrates do not affect it, a crucible of gold is consequently a valuable instrument in the analysis of minerals which require fusion with the caustic alkalies. The metal combines directly with fluorine, chlorine, and bromine, without the aid of heat, and with phosphorus when heated.

(1151) **Preparation of Fine Gold.**—Gold is best obtained in a state of purity by dissolving the metal in aqua regia, and evaporating the solution of auric chloride thus obtained with an excess of hydrochloric acid, for the purpose of destroying the excess of nitric acid: the solution is then largely diluted with water, to precipitate the argentic chloride, from which it is afterwards decanted. A solution of ferrous sulphate is next prepared and added to the solution of auric chloride: 1 part of gold requires between 4 and 5 parts of the crystallized sulphate: $6FeSO_4 + 2AuCl_3 = 2Fe_23SO_4 + Fe_2Cl_6 + Au_2$. Metallic gold is thus precipitated in the form of a finely-divided powder, which, when suspended in water, is brown by reflected, but purple when viewed by transmitted light. For commercial purposes it would be sufficient to collect the gold, dry it, and after fusing it with borax, to cast it into ingots; but when required to be perfectly free from silver, the gold is not melted at this stage, but the precipitated metal is boiled with hydrochloric acid of density 1·1. The acid is decanted, and the residue is boiled twice with fresh acid without washing the gold between these successive additions of acid. The last traces of iron and nearly all the argentic chloride are thus removed. A still better method is to pass a current of sulphurous anhydride through the solution of auric chloride, when the pure metal is precipitated in a much more coherent state: $2AuCl_3 + 3SO_2 + 6OH_2 = Au_2 + 3H_2SO_4 + 6HCl$. The gold is then washed, dried, and mixed with its own weight of hydric potassic sulphate, and fused in a Hessian crucible. The last portions of argentic chloride are thus removed, and the gold is perfectly pure. When thus prepared its surface often exhibits a crystalline

appearance, being embossed with aggregations of tetrahedra if the metal be allowed to cool slowly.

Levol prefers to precipitate the gold from an acid solution of its chloride by means of an acid solution of antimonious chloride: $3SbCl_3 + 2AuCl_3 = 3SbCl_5 + Au_2$. The hydrochloric solution retains any traces of argentic chloride which may be present.

(1152) **Uses of Gold.**—Gold is employed in its finely-divided state for gilding porcelain, which is first painted with an adhesive varnish and allowed to become partially dry; the powdered metal is then dabbed on with a dry pencil (having been previously mixed with a fusible enamel), after which the article is fired; the gilt portions are subsequently burnished, and take a high polish. It communicates a fine ruby colour to glass, and is the colouring ingredient in the beautiful red glass manufactured in Bohemia. The uses of gold in the fabrication of ornamental articles and in coinage are well known; like silver, it is too soft to be employed in a pure state.

(1153) **Gilding.**—Gilding on woodwork, papier-mâché, or plaster, is effected by means of gold-leaf, which is attached to the surface by an adhesive varnish, such as gold-size. Gilding upon metals is effected either through the medium of mercury, as in one of the processes for silvering (1123), or by voltaic action, as in the operation of electro-silvering already mentioned: for this purpose, a solution either of the aurous potassic cyanide, AuCy.KCy, or of aurous potassic sulphide, AuKS, is used (296).

With mercury, gold forms a semi-solid amalgam of a yellowish colour, which is soluble in an excess of mercury. This excess may be removed, as in the case of silver amalgam, by filtering, and squeezing it through chamois leather. It is this amalgam which is formed during the extraction of gold from its ores; it is also extensively prepared for the purposes of gilding. A combination of mercury with gold, Au_8Hg, may be obtained crystallized in brilliant four-sided prisms by acting with dilute nitric acid, aided by a gentle heat, upon an amalgam of gold containing about 1 part of gold to 1000 of mercury (T. H. Henry): these crystals are insoluble in nitric acid.

(1154) **Alloys of Gold.**—The ductility of gold is much impaired by alloying it with other metals, although its hardness and sonorousness are increased: these alloys are generally formed without difficulty. If a proportion of tin, cobalt, nickel, or zinc, greater than 2 per cent. of the mass be present in the alloy, it is unfit for coinage; and still smaller quantities of lead, arsenicum, antimony, or bismuth, render gold brittle. Palladium is a still

more inconvenient impurity, since it not only renders the gold brittle, but it requires special treatment in order to extract it, as it is not removed by the ordinary operations of the refiner. A similar remark is applicable to the alloy of platinum with gold. Small quantities both of platinum and of palladium render the gold nearly white. The native alloy of osmium and iridium, which frequently accompanies the Californian gold, does not combine with the metal, but remains disseminated through it in distinct grains after the gold has been melted. These grains occasion much inconvenience; they often escape notice until the metal passes through the coining press, where they make themselves apparent by their hardness, and the consequent injury of the dies.

Silver and gold may be alloyed with each other in all proportions. The alloy which they form has a pale greenish-yellow colour, but it becomes nearly white when the quantity of silver exceeds 50 per cent. The malleability of gold is less diminished by the presence of silver than by that of any other metal. In the arts it frequently becomes necessary to separate these two metals, and this is usually effected by the method termed *quartation* or *parting*. This operation depends on the solubility of silver in nitric acid, and the insolubility of gold in this liquid. It is necessary that the silver should amount to at least three times the weight of the gold, otherwise portions of silver would be protected mechanically from the action of the acid, and the separation would be incomplete. If, therefore, the alloy be found to contain more than a fourth of its weight of gold, sufficient silver is added to reduce it to this proportion, and hence the origin of the term 'quartation.' The metals are fused together, granulated by being poured into water, and then digested in the acid. The gold is afterwards melted into ingots, the silver is precipitated as chloride by common salt, and the chloride is reduced either by zinc (1128), or by fusion with an alkaline carbonate (1129). On the large scale sulphuric acid is usually substituted for nitric acid; it is much cheaper, and is quite as effectual in dissolving the silver if boiled with it (1141). Indeed, in refining upon the large scale, when sulphuric acid is used the gold may be obtained containing 998 or 999 thousandths of the pure metal; whereas when nitric acid is used, it is seldom finer than from 993 to 995 thousandths.

Silver and many other metals may also be removed from gold by forcing a current of chlorine gas through the melted metal; argentic chloride forms, and collects upon the surface, whilst the chlorides of arsenic, antimony, bismuth, and

zinc are volatilized if these metals are present (F. B. Miller): the argentic chloride formed in this manner, however, usually contains a comparatively large amount of gold, sometimes as much as 18 per cent. This process is now employed at the Royal Mint.

The most useful alloy of gold is that which it forms with copper; it is of a redder colour than pure gold, and considerably harder and more fusible, but it is less ductile and malleable. It is this alloy which is used for coinage. British standard gold contains 8·33 per cent. of copper, or 11 parts of gold to 1 part of copper. The density of this mixture is 17·157, instead of 18·47, the two metals expanding a little when they unite. In France and in the United States the standard gold contains 10 per cent. of copper. Jewellers frequently alloy their gold with a mixture of copper and silver. The alloys of gold and copper, when once the materials have been well mixed, do not exhibit the tendency to liquation which occasions so much trouble in the case of silver (1125). The solder used for uniting pieces of gold is an alloy of gold with copper, which melts at a lower temperature than pure gold.

(1155) **Assay of Gold.**—In the assay of gold, a combination of the processes of cupellation and quartation is employed. In the cupellation of gold the quantity of lead which is needed is about double that employed for silver: 1 part of copper requiring about 32 parts of lead. The assay of gold furnishes results which are more accurate than those obtained in the cupellation of silver. The loss of gold by volatilization is very much smaller, and scarcely any of the metal is carried into the cupel by an excess of lead.

The following is an outline of the method adopted in the assay of gold:—The quantity of the alloy for assay (usually 0·5 gram) having been accurately weighed, is wrapped in a piece of paper, with a proportion of silver equal to about 3 times that of the gold which the alloy is supposed to contain,* and this is

* An approximative estimate of the composition of the alloy is sometimes made by the use of the touchstone, although it is seldom employed by the practised assayer:—A number of pieces of alloy are formed containing known quantities of gold and copper, or of gold and silver: the first consisting of pure gold; the second of 23 parts of gold and 1 part of copper; the third of 22 of gold and 2 of copper, and so on: the assayer selects one of these alloys, or 'needles,' which from its colour he judges to approach nearest in composition to the alloy which he is about to assay: this he rubs upon a hard, black stone, the 'touchstone,' which is a peculiar kind of bituminous quartz formerly obtained from Lydia, in Asia Minor; black basalt, however, may be employed for the purpose: the alloy leaves a streak upon the stone, the colour of which is redder in proportion as the copper preponderates. The streak formed by the alloy for assay is then compared with that of the needles, until one of these is found to which it nearly cor-

submitted to cupellation in the manner already described when speaking of the assay of silver (1126). By this means the silver and the gold become thoroughly incorporated, and the copper is oxidized and absorbed by the cupel with the oxide of lead. The auriferous button is then hammered into a flattened disk, of about the size of a sixpence, and annealed by heating it to redness. It is next passed between a pair of laminating rollers, by which its thickness is reduced to that of an ordinary address card, after which it is a second time annealed. These operations render it sufficiently flexible to allow of its being coiled into a small spiral by rolling between the finger and thumb. The *cornet* thus obtained is next introduced into a flask which contains about 30 grams of nitric acid of density 1·180, heated nearly to the boiling-point. Brisk evolution of nitrous fumes immediately ensues; the silver is gradually dissolved away, and the gold is left in the form of the original cornet, as a brown, porous, very brittle mass. After this first boiling has been continued for 10 minutes, the flask is removed from the fire, the acid solution is poured off, and the cornet is washed by carefully pouring distilled water upon it; and this water, after standing for a couple of minutes, is again poured off. Some traces of silver are, however, still retained by the gold, and, in order to remove these, the cornet is again boiled with nitric acid, which, this time, must be of density 1·280. In this second boiling, which must be continued for 20 minutes, a small fragment of charcoal, such as a thoroughly charred pea, or a pellet of baked fireclay, should be introduced into the flask, in order to prevent the ebullition from taking place irregularly with sudden bursts, as it is very apt to do if this precaution be neglected.

The acid having been poured off, the flask is filled up completely with distilled water. A small, smoothly finished, porous clay crucible is placed over the mouth of the flask, and the flask and crucible are inverted, so that the cornet shall fall gently through the water into the crucible: by a dexterous movement of the hand, the flask is then withdrawn in such a manner as to prevent the overflow of any liquid from the little crucible; the water is afterwards carefully poured off from the cornet, and the crucible is heated to redness in the muffle. By this means the gold, although it is not fused, is rendered much more compact;

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responds. The judgment may be further aided by moistening the streaks obtained with a little nitric acid, which dissolves the copper or silver, but leaves the gold.

it shrinks in bulk, loses its brown appearance, and assumes the peculiar colour and lustre of the metal. When cold, the cornet is weighed with the same precision as the original alloy. The assayer calls the arbitrary weight of the alloy upon which he operates, 1000; his weights are all subdivided so as to give him the value of the alloy in thousandths of this original quantity: so that if he find a portion of the alloy which originally weighed 1000 of these arbitrary units, to yield a quantity of gold equal to 916·6 of these parts, he reports it as 916·6. 1000 ounces of such an alloy would contain 916·6 ounces of fine gold.

The amount of alloy upon which it is most convenient to operate in assaying is half a gram, or between 7 or 8 grains.

The gold contained in the cornet is never absolutely pure: it retains small quantities of lead and silver, and frequently also traces of copper, which render its weight a little higher than it ought to be. In order to ascertain the amount of this error, a number of *proofs* are passed through the muffle simultaneously with the alloys, and subjected to the same process as the alloys themselves. These proofs consist of weighed portions of fine gold, to each of which is added a proportion of copper equal to that estimated to exist in the alloys under examination. The excess of weight which these proofs indicate shows the amount of the correction which it becomes necessary to make. This correction is liable to daily variation, according to the temperature of the furnace, the more or less perfect softening of the buttons during annealing, the thickness of the cornets, &c.; but it usually varies from 0·2 to 0·5 parts in 1000. Many assayers vary the quantity of lead according to the proportion of copper in the alloys, but it is more advantageous to use the same amount of lead in all cases; the correction then becomes uniform for all the assays passed at one operation.

When the alloy contains very little copper, as commonly occurs with native gold, the button of alloy is liable 'to spit' as it cools after the cupellation; this may easily be prevented by the addition of a small fragment of copper, not exceeding 50 milligrams in weight, before introducing the alloy into the cupel.

It frequently happens that it is necessary to ascertain the proportion both of gold and of silver in a given alloy. If the proportion of gold preponderate, the quantity of gold is determined in the manner above described, and that of the gold and silver together is ascertained by submitting a portion of the alloy to cupellation with lead, as if it consisted of silver only (1126). The two metals, gold and silver, remain upon the cupel, whilst the copper and more oxidizable metals are absorbed. The weight of the residual button gives the united weight of the gold and silver, and the difference between this weight and that of the gold alone will of course furnish the proportion of silver.

When the proportion of gold is very small compared with that of the silver, the two metals are treated with nitric acid at once, without submitting them to the usual assay for gold; the acid dissolves the silver and other metals which may be present, leaving the gold in the form of a black powder: this powder must be collected by subsidence in one of the small porous crucibles used for annealing gold cornets, in which it is ignited, and can afterwards be weighed without difficulty.

(1156) **AUROUS CHLORIDE**, or *Protochloride of gold*; AuCl=232·1.—Gold forms three compounds with chlorine—a protochloride, AuCl, a dichloride, Au_2Cl_4 or $AuCl_3.AuCl$, and a trichloride, $AuCl_3$. When auric chloride is exposed to a gentle

heat, it fuses, without undergoing decomposition, but if the temperature be raised to 185° (365° F.) chlorine is gradually expelled, and a pale yellow, sparingly soluble powder is left, which is the protochloride. It is an unstable compound, but it may be washed with cold water to remove any undecomposed trichloride; boiling water converts it into a mixture of the trichloride with metallic gold, and a similar change is produced by exposing it to light, or even by long-continued washing with cold water. If the temperature be raised somewhat above 200° (392° F.), the whole of the chlorine is expelled. Aurous chloride, when digested in a solution of potassic hydrate, yields hydrated aurous oxide and potassic chloride.

(1157) **AUROUS-AURIC CHLORIDE**, or *Dichloride of gold*; Au_2Cl_4 or $AuCl_3.AuCl = 535{\cdot}2$.—This compound is easily obtained, according to Thomsen (*Jour. pr. Chem.*, 1876, [2], xiii. 337), by the action of chlorine on spongy gold, such as is obtained by precipitation with sulphurous acid. It is dark-red and very hygroscopic, being decomposed by the action of water into auric chloride, which dissolves, and aurous chloride. At 250° (482° F.) it is decomposed, metallic gold being left, whilst chlorine escapes and some anhydrous trichloride sublimes.

(1158) **AURIC CHLORIDE**, or *Trichloride of gold*; $AuCl_3 = 303{\cdot}1$; *Comp. in* 100 *parts*, Au, 64·86; Cl, 35·14.—This compound is produced when the metal is dissolved in aqua regia; on evaporating the solution to dryness at a temperature not exceeding 120° (248° F.), taking care to maintain the hydrochloric acid in excess over the nitric, this salt remains behind as a dark red, deliquescent mass; but usually a portion of the trichloride is reduced to the state of insoluble protochloride, for it is difficult to get rid of the last portion of acid without decomposing part of the salt. It may readily be obtained in a pure state, however, by decomposing the dichloride with a small quantity of water, heating gently, and filtering from the aurous chloride; on concentrating the solution, large dark orange-coloured crystals of the hydrate, $AuCl_3.2OH_2$, are deposited, which lose their water of crystallization in dry air, and leave the anhydrous chloride, $AuCl_3$. When heated to somewhat above 200° (392° F.), it is resolved into metallic gold and aurous chloride, whilst at higher temperatures all the chlorine is given off, and nothing but metallic gold is left; nevertheless, auric chloride sublimes in long needles, when gold-leaf is heated at 300° (572° F.), in a current of chlorine. It is very hygroscopic, and forms with water an orange-coloured solution, which preserves its colour

even when very largely diluted; alcohol also dissolves the trichloride, and ether takes it up so freely as to separate it from its aqueous solution when agitated with it. Auric chloride forms a crystalline compound with hydrochloric acid, $AuHCl_4.4OH_2$; it also unites with the chlorides of many of the basylous metals to form double salts; that with potassium crystallizes in efflorescent, striated prisms, consisting of $2(KCl.AuCl_3).5OH_2$; that with sodium forms four-sided prisms, $NaCl.AuCl_3.2OH_2$; with ammonium, $NH_4Cl.AuCl_3.OH_2$. The chlorides of most of the organic bases also form crystallizable double salts with auric chloride, so that these compounds are often employed to determine the combining number of the organic alkali. Auric chloride is easily reduced by many substances; the reaction of ferrous sulphate in presence of an excess of acid has already been mentioned, so likewise has that with sulphurous anhydride, and with antimonious chloride (1151). Oxalic acid produces a similar precipitate of metallic gold even in acid solutions: thus, $2AuCl_3+3H_2C_2O_4=Au_2+6HCl+6CO_2$: the powder, when viewed by reflected light, appears to be of a brown colour, but if suspended in water it gives a purple tint by transmitted light. Many organic substances also exert a reducing effect upon auric chloride; hence the fingers, or writing-paper, if washed over with the solution, become stained of a violet colour when exposed to the sun's light. Metallic gold is also readily obtained from the solution of this salt by other means. Phosphorous and hypophosphorous acids, and solutions of their salts, produce this effect; and a similar result is obtained by contact with many of the metals, such as mercury, copper, iron, and zinc. A stick of phosphorus when immersed in a solution of auric chloride soon becomes coated with the reduced metal; and if a few drops of a solution of phosphorus in ether, or in carbonic bisulphide, be mixed with a very dilute solution of neutral auric chloride, containing from 30 to 60 mgrms. of the metal in a litre of water, the gold will be reduced in the course of a few hours. Provided that the bottle containing the solutions be chemically clean, the metal will be separated in particles of such extreme tenuity that it will remain suspended in the liquid for months, giving to it a ruby red or amethystine colour when viewed by transmitted light, although it appears to be turbid and brown when seen by reflected light. If this red liquid be mixed with a small quantity of a solution of common salt, the ruby tint is immediately changed to purple; in consequence of the state of aggregation of the metal being changed; the liquid then

becomes colourless in a few hours, and the whole of the suspended particles of gold are deposited as a purple-coloured, metallic powder (Faraday).

(1159) **BROMIDES OF GOLD.**—Three bromides of gold analogous to the corresponding chlorides are known—namely, aurous bromide, AuBr, dibromide of gold, Au_2Br_4 or $AuBr_3.AuBr$, and auric bromide, $AuBr_3$.

Aurous Bromide, or *Protobromide of gold,* AuBr = 276·6.—This is obtained as a yellowish-grey mass when hydric auric bromide, $AuHBr_4.5OH_2$, is heated at 115° (239° F.) for some time, with occasional stirring. Treated with hydrobromic acid it is resolved into metallic gold and hydric auric bromide.

Aurous-auric Bromide, or *Dibromide of gold,* Au_2Br_4, is an almost black compound prepared in a manner analogous to the corresponding chlorine compound by acting on spongy gold with bromine.

Auric Bromide, or *Tribromide of gold,* $AuBr_3$ = 436·6.—This may be obtained from the dibromide by treating it with ether in the cold, whereby it is decomposed, auric bromide dissolving in the ether. On evaporation at a low temperature, the anhydrous salt is left in large crystals. It is very soluble in water. An aqueous solution of auric bromide may easily be prepared by agitating the dibromide with warm water. *Hydric auric bromide,* $AuHBr_4.5OH_2$, is a very stable compound, crystallizing in large acicular prisms of a deep cinnabar colour, which melt in their water of crystallization at 27° (80°·6 F.). It is easily prepared by adding bromine to spongy gold, and when the reaction has subsided, 1 mol. of hydrobromic acid (density 1·38) for each atom of gold, and then bromine until the whole is perfectly dissolved. On standing for some time the mixture solidifies to a crystalline mass of the new compound. Auric bromide forms numerous double salts.

(1160) **IODIDES OF GOLD.**—There are two iodides of gold, corresponding to the chlorides. Aurous iodide, AuI, is a yellow insoluble powder. The auric iodide, AuI_3, is unstable; it is green and sparingly soluble; it forms double salts with the iodides of the alkali-metals.

(1161) **AUROUS OXIDE,** or *Suboxide of gold;* Au_2O=409·2. —There are two oxides of gold: a suboxide, Au_2O, and a sesquioxide, Au_2O_3; the suboxide is obtained as a dark green powder by precipitating aurous chloride with a dilute solution of potassic hydrate; it is slightly soluble in excess of the alkali: when digested with ammonia it forms fulminating gold: hydrochloric acid converts it into metallic gold and auric chloride. Aurous oxide remains in suspension in pure water, and passes through the filter; but boiling the solution after adding any saline compound causes its precipitation.

(1162) **AURIC OXIDE,** or *Peroxide of gold;* Au_2O_3=441·2. —This compound is best obtained by decomposing a solution of auric chloride by magnesia; for if solutions of the alkalies be used, they adhere strongly to the precipitate: it falls in combination with the earth, which may be removed by means of dilute nitric acid, and auric oxide remains as a yellow hydrate, $Au_2O_3.3OH_2$, if the acid used be weak, or as a brown anhydrous

powder if strong. It may also be obtained very conveniently by adding sodic hydrate (3 mols.) to a very dilute solution of auric chloride (1 mol.) and gently heating: the solution acquires a dark brown colour, and on adding a concentrated solution of sodic sulphate the hydrated oxide is precipitated. Auric oxide is very readily reduced by exposure to light, and at a temperature of about 245° (473° F.) it is resolved into metallic gold and free oxygen. It is taken up by strong nitric and sulphuric acids, but the sesquioxide is deposited again from these solutions in a pure state when they are diluted and allowed to stand for a long time; the sulphuric acid solution, however, never becomes entirely decomposed. Auric oxide is dissolved by hydrochloric, hydrobromic, and hydriodic acids, forming auric trichloride, tribromide, or triiodide.

Hydrated auric oxide possesses acid properties, and is sometimes termed *auric acid.* It is readily acted on by the alkaline hydrates, forming salts which have been termed *aurates;* they are soluble in water, and form yellow solutions. *Potassic aurate* crystallizes in yellowish needles, $KAuO_2.3OH_2$; its solutions may be used in electro-gilding. Most of the compounds of auric acid with the earths and other metallic oxides are insoluble.

Auric oxide forms with ammonia a dark olive-brown fulminating compound, analogous to that furnished by silver (1138); the same compound may be formed by adding ammonia to the trichloride, but in this case it is of a reddish-yellow colour, owing to the admixture of a little ammoniacal subchloride of gold. So great is the attraction of auric oxide for ammonia, that it decomposes the neutral salts of ammonium, such as the sulphate, and sets the acid at liberty.

(1163) **SULPHIDES OF GOLD**; $Au_4S_4=914{\cdot}4$.—When a current of sulphuretted hydrogen is passed through a solution of auric chloride, a black precipitate is produced, which, according to Levol, is a disulphide, or rather $Au_3S.Au_2S_3$. It is soluble in the solutions of the sulphides of the alkali-metals: its solution in disodic sulphide yields a colourless salt which is soluble in alcohol; it crystallizes in six-sided prisms, consisting of $NaAuS.4OH_2$ (Yorke), $Au_4S_4+4Na_2S$ becoming $4AuNaS+2Na_2S_2$.

Auric Sulphide; $Au_2S_3=489{\cdot}2$.—This is obtained as a deep yellow, flocculent precipitate on passing sulphuretted hydrogen through a cold, dilute solution of auric chloride. If finely-divided gold be heated with sulphur in contact with potassic carbonate, a double sulphide of gold and potassium is formed; it resists a red heat, and is very soluble in water: this sulphur salt is used for

gilding china, and produces the colour known as *Burgos lustre.* According to Muir, a double sulphide of gold and silver of the formula, $2Au_2S_3.5Ag_2S$, is formed by the action of molten sulphur on a mixture of gold and silver in a fused state.

(1164) **Purple of Cassius.**—When a mixture of stannous and stannic chloride very much diluted is added drop by drop to a dilute neutral solution of auric chloride, a purple, flocculent deposit is produced. The same compound is readily formed by digesting metallic tin in a neutral solution of auric chloride; metallic gold and the purple of Cassius being formed. The true nature of this compound has been the subject of much discussion. Berzelius concluded from the researches of Figuier (*Ann. Chim. Phys.*, 1844, [3], xi. 354) that it consists of a hydrated double stannate of gold and tin, $Sn''Au_2Sn_2O_6.4OH_2$. Purple of Cassius remains in suspension in pure water, and passes through the filter, but is separated on adding a soluble salt to the liquid and boiling it. It is insoluble in solutions of potassic and sodic hydrates, but soluble in ammonia, forming a deep purple liquid, from which it is deposited unchanged if the ammonia be expelled by heat, or neutralized by an acid. This solution is bleached by the action of light, and gold is deposited. Purple of Cassius is decomposed by the acids, metallic gold being left; but it is not changed by the action of light. If heated to redness water is expelled, and a red powder is left, which is a mixture of metallic gold and stannic oxide. Purple of Cassius, when mixed with a little borax or some fusible glass, and applied to the surface of china, imparts to it a tint varying from a beautiful rose to a rich purple colour. It is this compound which is used as the colouring material in the red glass of Bohemia.

(1165) **Characters of the Salts of Gold.**—The salts of gold are recognized by the brown precipitate of metallic gold produced by *ferrous sulphate* in their acidulated solutions in the absence of free nitric acid; and by the formation of the purple of Cassius on adding to the neutral solution a dilute mixture of *stannous* and *stannic chloride. Metallic tin* yields the same precipitate, and is a still more delicate test. Salts of gold are reduced to the metallic state by boiling their acidulated solutions with a soluble *oxalate, formate,* or *sulphite. Mercurous nitrate* also gives a dark brown precipitate of reduced gold. All the salts of gold are decomposed when ignited in the open air.

(1166) **Estimation of Gold.**—Gold is always estimated in the metallic state. It may be readily separated from all the preceding metals by precipitating its solution by means of a solution of

ferrous sulphate, after acidulating it with hydrochloric acid. The precipitate is collected upon a filter, ignited, and weighed as pure gold.

§ IV. PLATINUM: Pt=197·1.

(1167) **PLATINUM:** *Density,* 21·5; *Fusing-pt.* 1460° (2660° F.); *Dyad, in Platinous salts, as* $PtCl_2$; *Tetrad in Platinic salts, as* $PtCl_4$.—This metal, which is named from the Spanish *Platina,* '*little silver,*' is found in but comparatively few places; it was not recognized as a separate metal until Wood, an assayer of Jamaica, in 1741, pointed out its distinctive characters. It always occurs in the native state, usually in small flattened grains, in which it is mixed with palladium, rhodium, osmium, ruthenium, and iridium,—metals which are rarely found except when associated with platinum. Occasionally it occurs in larger nodules, frequently alloyed with gold, and traces of silver, and with copper, iron, and lead: it is said always to be present in small quantity in native silver. The deposits of platinum are for the most part met with in alluvial districts associated with the débris of the earliest volcanic rocks: it has not as yet been seen in the rock, but from the materials which accompany it, this is generally supposed to have been serpentine. Platinum is chiefly supplied from the mines of Mexico, of Brazil, of Ceylon, and of the Ural Mountains: it has also been met with in California and Australia. It is separated, by washing, from the lighter impurities contained in its ore.

(1168) **Extraction of Platinum.**—On account of the extreme infusibility of platinum, it requires a mode of manipulation which is complicated and peculiar. 1. The method contrived by Wollaston is as follows:—The ore, which usually contains from 75 to 85 per cent. of platinum, is treated separately first with nitric acid, and then with hydrochloric acid, in order to remove the more easily oxidizable metals, after which it is digested at a moderate heat in diluted aqua regia as long as anything is dissolved, the solution of the platinum taking place very slowly. It is best therefore to place the ore in hydrochloric acid, and add small quantities of nitric acid at intervals to maintain the action, taking care to maintain a sufficient excess of hydrochloric acid. The clear liquid is then decanted, and the residue again treated with fresh acid as long as anything is dissolved: into the mixed acid solutions a solution of ammonic chloride in 5 times its weight of water is poured (41 parts of the salt to 100 of ore); the greater

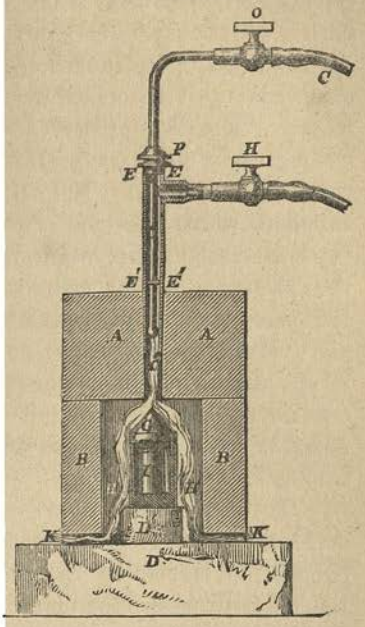
part of the platinum is thus precipitated in the form of a yellow double salt, $2NH_4Cl.PtCl_4$, which is sparingly soluble. A slight modification of Wollaston's process is now generally employed, the solutions being evaporated to dryness before precipitation with ammonic chloride, and heated for some time at 125° (257° F.), whereby the palladium and iridium are converted into subchlorides, which remain undissolved on treating the mass with water. The solution after being acidified with hydrochloric acid is precipitated with ammonic chloride in the manner already described. The mother-liquor still retains a portion of platinum, which is precipitated by means of metallic iron; the black powder is redissolved in aqua regia, and treated in the same way as the original solution, the precipitate thus obtained being added to the first crop. The ammonic platinic chloride is then washed, and heated to redness, by which means the ammonia and chlorine are expelled, leaving the platinum behind in porous, slightly coherent masses; this *spongy platinum* is powdered in a wooden mortar and rubbed into a magma with water, in which state it is thoroughly washed; the metallic particles soon subside, and the lighter impurities are carried away.* This metallic mud is next poured into a somewhat conical brass mould, closed below with blotting-paper loosely supported by a plug: the greater part of the water drains off, after which the whole is subjected to the action of a very powerful press. The mass, previously of a dull grey colour, now assumes a compact metallic appearance, and acquires a density of about 10; it is next exposed to an intense heat in a wind furnace, and the ingot is forged by hammering it upon its two ends,—never upon its sides, as if this were done it would split. This heating and forging is several times repeated until the mass becomes homogeneous and ductile, when it has a density of about 21·5. Wollaston's process for working platinum depends upon its property of welding at very high temperatures. Deville and Debray, in their important memoir on platinum and the metals which accompany it (*Ann. Chim. Phys.*, 1859, [3], lvi. 385), recommend the fusion of the platinum by means of the oxyhydrogen blowpipe, in a cavity formed in a mass of lime, for the purpose of freeing commercial platinum from the silicon and osmium which it always contains.

The apparatus consists of the blowpipe, c, fig. 374, a furnace, A B D, and a

* Platinum thus prepared usually retains a small quantity of iridium, which accompanies the ammonic platinic chloride. The platinum may be freed from this impurity by the method described in paragraph (1212).

crucible, G H I. The blowpipe is composed of a copper tube 12$^{mm.}$ in diameter, terminating below in a slightly conical platinum jet 40$^{mm.}$ (about an inch and a half) long. Within this tube, which is supplied with hydrogen through the stopcock, H, is a second copper tube, c′, terminated also by a platinum nozzle with an aperture of from 2 to 3$^{mm.}$ in diameter.

FIG. 374.

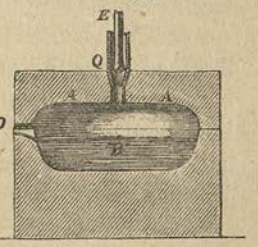


The furnace, A B D, consists of three pieces of well-burnt lime of slightly hydraulic quality, which can be turned in a lathe with ease. The cylinder, A, is about 60$^{mm.}$ thick, and is perforated with a slightly conical tube, into which the blowpipe fits accurately, and is allowed to pass about half-way through the thickness of the mass. A second somewhat deeper cylinder of lime, B, is hollowed into a chamber sufficiently wide to admit the crucible and leave an interval of not more than 3 or 4$^{mm.}$ clear around it. At K K are four apertures for the escape of the products of combustion.

The outer crucible, H, H, is also made of lime, but it contains a smaller crucible, I, of gas-coke, provided with a cover of the same material, and in this the substance to be fused is placed, the crucible resting on the lime-support, D′. The conical cover, G, is made of lime, and its apex should be placed exactly under the blowpipe jet, at a distance from it of from 20 to 30$^{mm.}$ or about an inch.

The different pieces of the furnace must be bound round with thin iron wire to support them when they crack. The oxygen is admitted under a pressure of a column of 40$^{cm.}$ (16 inches) of water. The temperature is gradually raised to the maximum, and in about 8 minutes from this time the experiment is complete.

FIG. 375.



By employing a jet of mixed coal-gas and oxygen (E Q, fig. 375) in a furnace of lime, A B, provided with lip at D for pouring, Deville and Debray succeeded at an expense of about 1400 litres of oxygen or about 43 cubic feet, in melting and refining in 42 minutes, 11·595 kil. (25·4 lb. avoirdupois) of platinum, and casting it into an ingot in a mould of gas-coke; and much larger masses have since been melted by this method. Lime is so bad a conductor of heat, that, if a cup of lime not more than 20$^{mm.}$ thick be filled with melted platinum, the exterior scarcely rises beyond 150° (302° F.).

2.—Deville and Debray introduced a different method for the extraction of platinum from its ores, but it is not employed to any extent in the platinum industry, the modification of Wollas-

ton's method previously described being usually preferred. In Deville and Debray's dry process a small reverberatory furnace, the bed of which is composed of a hemispherical cavity of fire-brick, lined with clay, is heated to full redness, and a charge consisting of 100 kilos., or 2 cwt. of the platinum ore, mixed with an equal weight of galena, is added in small quantities, stirring with iron rods until the platinum and lead ore have combined into a matt. A small quantity of glass is thrown in to act as flux, and by degrees a quantity of litharge equal in weight to the galena employed is added. The sulphur is thus completely oxidized and expelled, whilst the lead of the galena and the litharge is reduced to the metallic state, when it forms an easily fusible alloy with the platinum. The melted mass is now left completely at rest for some time. The osmide of iridium (which is not attacked at all during the operation) gradually sinks to the bottom of the liquid alloy, and the upper portions of the platiniferous lead are cautiously decanted from it by iron ladles, and cast into ingot moulds. The residue, containing the osmide of iridium, is added to a subsequent melting.

The platiniferous lead is then submitted to cupellation in the ordinary manner, and the crude metallic platinum left after cupellation is refined by fusion on a bed of lime, by means of the oxyhydrogen blowpipe: after undergoing this operation it furnishes a ductile and malleable alloy of platinum with some of the metals which accompany it.

The alloy of platinum, iridium, and rhodium is well adapted to the preparation of crucibles, for if the proportions of the metals be properly adjusted, this alloy is harder and resists a higher temperature than pure platinum; at the same time it is less easily attacked by chemical agents. Such an alloy may be obtained from the crude platinum ore by simply fusing it by the oxyhydrogen blowpipe upon a bed of lime with a quantity of lime equal in weight to the amount of iron in the ore. Palladium and osmium are volatilized during this process of fusion, whilst the copper and iron become oxidized, and form fusible compounds with the lime.

Platinum as it occurs in commerce is a complex alloy containing small quantities of many other metals, from which it can be freed only by a long and tedious process (comp. Deville and Debray, *Compt. Rend.*, 1875, lxxxi. 839).

(1169) **Properties of Platinum.**—Platinum is a white metal susceptible of a high lustre, and when pure is about as hard as copper. In ductility it rivals iron, and in tenacity it is inferior

only to iron, cobalt, and nickel, and perhaps copper. It resists the highest heat of the forge, but it may be fused by the voltaic battery or by the oxyhydrogen blowpipe, and may even be volatilized and dispersed with scintillations. Deville and Debray state that it absorbs oxygen, and if melted in considerable masses spits like silver on rapidly cooling. Attempts to crystallize platinum artificially have not succeeded, but very perfect octahedra have been met with in its native beds. The density of commercial platinum differs somewhat with the mode of manipulation to which it has been subjected, but the pure cast-metal, according to Deville and Debray, has a density of 21·5, being (with the exception of iridium and osmium, which are equally dense) the heaviest form of matter as yet known. It expands less by heat than any other metal, and in its power of conducting heat and electricity it is much inferior to gold and silver, ranking very near to iron in these respects.

Platinum does not undergo oxidation in the air at any temperature: the acids have scarcely any perceptible effect upon it; but Scheurer-Kestner states that boiling sulphuric acid dissolves it in minute quantity; if nitrous acid is present it is much more readily attacked, and a mixture of nitric and hydrochloric acids dissolves it, although but slowly. If heated to redness in the air in contact with caustic alkalies or alkaline earths, especially with hydrate of lithia or with baryta, it is corroded, owing to the formation of an oxide which combines with the alkaline base. When phosphorus is heated with spongy platinum, the two combine readily: the attraction of sulphur for platinum is much less powerful, whilst dry chlorine is without action upon this metal, even when aided by heat. It dissolves in a concentrated solution of potassic cyanide, with evolution of hydrogen.

(1170) **Platinum Black.**—Platinum may be obtained in a state of subdivision still finer than that in which it is left on heating the ammonic platinic chloride. In this form it has the appearance of soot, and is termed *platinum black*. It may be procured in this condition by several methods, of which one of the best consists in dissolving platinous chloride in a strong solution of potassic hydrate, and adding alcohol to the hot liquid which is placed in a capacious vessel, and kept constantly stirred; brisk effervescence takes place, owing to the escape of carbonic anhydride; the platinum is reduced, and is deposited as a black powder, which requires repeated washing,—first with alcohol, next with solution of potassic hydrate, then with hydrochloric acid, and lastly with water. It may also be obtained from potassic platinic chloride by reducing it at a temperature of 250° (482° F.), in an atmosphere of hydrogen or of coal-gas, and thoroughly washing the product. A very energetic form of platinum black is obtained on adding a solution of platinic chloride to a boiling mixture of 3 parts of glycerin with 2 of a solution of potassic hydrate, density 1·08. On boiling platinic chloride with a solution of potassic sodic tartrate (Rochelle salts) carbonic anhy-

dride is evolved, and the whole of the platinum is precipitated in a finely-divided state. Platinum, in this finely-divided state, condenses oxygen within its pores with the greatest readiness, absorbing many times its bulk of the gas from the air. If moistened with alcohol or ether it imparts this oxygen to them, and forms new compounds, whilst the powder glows from the heat which is developed. In all its states, platinum possesses, in a marked degree, this property of condensing gases upon its surface; and the more finely it is divided, and consequently the larger the surface which it presents, the more striking is the phenomenon.

(1171) **Uses of Platinum.**—The most important applications of platinum are confined to the laboratory of the manufacturing and experimental chemist; they depend upon its great infusibility, and its power of resisting chemical agents. Its introduction as a material for the construction of apparatus employed by the analytical chemist has contributed in no small degree to the rapid progress of the science during the last forty or fifty years, by conferring upon its experiments a precision, neatness, and accuracy till then unattainable. In the concentration of oil of vitriol, large platinum stills are frequently employed; some of these vessels weigh upwards of 1000 ounces, or 28·4 kilos. It is found expedient to gild these vessels upon their inner surface, for, unless this precaution be adopted, the stills when made of platinum prepared by Wollaston's method, after a short time, become sufficiently porous to allow the acid to transude. An attempt was made in Russia to employ platinum for coinage, but it was found to be inconvenient, and the experiment has been abandoned. Platinum is sometimes used for the touch-holes of fowling-pieces.

(1172) **Alloys of Platinum.**—Platinum may easily be alloyed with many of the more fusible metals, the combination generally taking place with development of light and heat. These alloys are much more fusible than pure platinum: care must therefore be taken not to heat the oxides of easily reduced metals, such as lead or bismuth, in platinum crucibles, as if the oxide should happen to be reduced, the crucible would be destroyed by the formation of a fusible alloy. Most of the platinum of commerce contains iridium, which, without impairing its power of resisting chemical agents, increases its hardness and durability. It is remarkable, that although pure platinum is perfectly insoluble in nitric acid, yet when alloyed with 10 or 12 times its weight of silver, both metals are dissolved by the acid: a somewhat similar phenomenon takes place with an alloy of platinum and copper; and in a less degree with alloys of that metal with zinc, bismuth, or lead. An amalgam of platinum may be formed by acting upon an amalgam of sodium with a neutral solution of sodic

platinic chloride, $2NaCl.PtCl_4$; and, according to Levol, when this amalgam is attacked by nitric acid, the platinum is partially dissolved, together with the mercury.

Platinum enters into combination with carbon and with silicon: sometimes in the fusion of ordinary platinum wire before the blowpipe, the globules of the melted metal become covered with a film of colourless glass, arising from the oxidation of the silicon and the fusion of the resulting silica. A brittle granular compound of platinum and silicon was accidentally obtained by Daniell, owing to the action of the silicon at a high temperature upon one of the platinum bars of his pyrometer. It appeared to be formed by a kind of cementation, the silicon being derived from the clay of the envelope in which the bar was heated: the proportion of silicon amounted to 1·5 per cent. A fusible compound of platinum with boron was also obtained by Wöhler and Deville.

(1173) **PLATINOUS CHLORIDE**; $PtCl_2 = 268·1$.—There are two compounds of platinum with chlorine, platinous chloride, $PtCl_2$, and platinic chloride, $PtCl_4$. In order to obtain the platinous chloride, formerly known as the protochloride, the solution of platinum in aqua regia should be evaporated, and the residue exposed to a heat of 235° (455° F.), as long as any chlorine is expelled; the compound which remains is platinous chloride. It is of an olive colour, and is insoluble in water: it is scarcely acted upon by nitric or sulphuric acid, but hydrochloric acid dissolves it when warmed: it is easily soluble in potassic hydrate, and in platinic chloride; with the latter it forms a double salt, of so deep a brown colour as to appear opaque in a concentrated solution. It forms crystallizable double salts with the chlorides of the alkali-metals. The potassic salt, $2KCl.PtCl_2$, which is readily soluble, is easily obtained from potassic platinic chloride, $2KCl.PtCl_4$, by mixing the finely powdered salt with a small quantity of hot water, heating, and adding cuprous chloride until the greater part of the platinic salt is dissolved: on filtering from the undissolved salt and allowing the solution to cool, *potassic platinous chloride* is deposited in red prisms.

(1174) **PLATINIC CHLORIDE**, or *Tetrachloride*; $PtCl_4 = 339·1$, formerly *bichloride of platinum*; *Comp. in* 100 *parts*, Pt, 58·12; Cl, 41·88.—This salt is obtained by dissolving platinum in aqua regia, and evaporating the solution to dryness by means of a steam heat.* It is a deliquescent salt, which may

* In an active laboratory a number of residues containing platinum gradually accumulate, and these may be turned to account in the following manner:—The solutions, mixed with the precipitates, are evaporated to dryness, and transferred to a clay crucible, in which they are heated strongly, with free access of air, in order to burn off organic matters; after which the residue is boiled with hydro-

be obtained crystallized in prisms, having the formula $PtCl_4 10OH_2$: these are soluble in water, yielding a deep orange-coloured solution; it is also freely dissolved by alcohol and by ether. When a solution of platinic chloride in hydrochloric acid is evaporated over lime and sulphuric acid, large, brownish red, deliquescent crystals, containing $2HCl.PtCl_4.6OH_2$, are obtained. When heated at 235° (455° F.), it loses half its chlorine, forming platinous chloride, and if the temperature be further raised, it is completely decomposed, and metallic platinum is left. Platinic chloride may easily be reduced to a platinous salt by passing sulphurous acid through a boiling solution of the salt containing hydrochloric acid in excess; by excess of sulphurous acid the solution is slowly rendered colourless, when it contains platinous sulphite, and free hydrochloric acid.

Platinic chloride forms numerous double salts with other chlorides; they may be obtained by mixing the solutions of these chlorides with that of the tetrachloride, and evaporating. *Potassic platinic chloride* ($2KCl.PtCl_4 = 488{\cdot}3$; density, 3·586) is a sparingly soluble, anhydrous compound, which crystallizes in octahedra; it is insoluble in alcohol and in ether. The salt is commonly used as a means of determining analytically the quantity of potassium in a compound: 100 parts of this salt contain Pt, 40·36; K, 16·02 = K_2O, 19·29. It is decomposed by a red heat into potassic chloride and metallic platinum, chlorine escaping. *Sodic platinic chloride*, $2NaCl.PtCl_4.6OH_2$, crystallizes in beautiful red striated prisms, which are soluble in water, alcohol, and ether. *Ammonic platinic chloride* ($2NH_4Cl.PtCl_4 = 446{\cdot}1$; density, 3·009) is very similar in appearance to the corresponding potassic salt, with which it is isomorphous; it is sparingly soluble in water, and is insoluble in alcohol and in ether. This salt is employed in analysis for determining the quantity of ammonia present in solution; 100 parts of this salt contain, Pt, 44·18, and NH_3, 7·62. It is also used for separating platinum from the other metals with which it is associated, after they have been brought into solution by treating the ore with aqua regia (1167). When ammonic platinic chloride is ignited, the ammonium and chlorine are wholly expelled, and pure platinum remains in the spongy form. When treated with sulphurous acid, the platinic chloride in the salt is reduced to platinous

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chloric acid, then with water, and lastly with nitric acid; a thorough washing with water follows. The impurities having thus been removed, the residual platinum may be converted into tetrachloride by means of aqua regia.

chloride, and a compound, $2NH_4Cl.PtCl.HSO_3.OH_2$, a salt of *platino-chlorosulphurous acid*, is obtained, which yields crystalline salts with bases, the hydrogen in the HSO_3 being replaced by the metal; the sodic salt crystallizes in orange-coloured needles of the formula, $2NH_4Cl.PtCl.NaSO_3.OH_2$ (Birnbaum, *Ann. Chem. Pharm.*, 1871, clix. 116).

(1175) **Basic Compounds of Platinum.**—The action of ammonia upon platinous chloride gives rise to the formation of several remarkable compound bases, the composition of which offers considerable interest in a theoretical point of view. Magnus found that if platinous chloride is dissolved in hydrochloric acid, the addition of an excess of ammonia to the boiling solution causes the deposition of brilliant, green, acicular crystals which are insoluble in water and in hydrochloric acid: they contain the elements of 2 molecules of platinous chloride, and 4 of ammonia, $N_4Pt_2''H_{12}Cl_4$. This compound, however, undergoes no change when digested at ordinary temperatures in solutions of the alkaline hydrates, or in the concentrated acids, but when boiled with them it is slowly decomposed. If digested with dilute nitric acid, one-half of the platinum is separated as nitrate, and on evaporating the solution, a salt is obtained in small, brilliant, flattened prisms of the chloronitrate, $Cl_2Pt^{iv}(NH_2.NH_4)_2(NO_3)_2$, or $N_4PtH_{10}Cl_2.2HNO_3$. Neither the chlorine nor the platinum can be detected in this solution by the usual tests. The nitric acid may be displaced in it by double decomposition with sodic sulphate, phosphate, or oxalate, and a sparingly soluble sulphate, phosphate, or oxalate of the platinum base is then formed. The base of these salts (commonly called *Gros's* salts, from the name of their discoverer) has not been isolated.

Raewsky discovered that if the green salt of Magnus be boiled with concentrated nitric acid, red fumes are disengaged, and a different salt is formed, which may be obtained in crystals on evaporation. The nitric acid in this compound may be displaced by an equivalent quantity of oxalic or of carbonic acid.

Raewsky's nitrate may also, according to Hadow, be formed readily by boiling Gros's nitrate for some hours with a solution of argentic nitrate and nitric acid, by the following reaction, $2(N_4PtH_{10}Cl_2.2HNO_3) + 2AgNO_3 + OH_2 = N_8Pt_2H_{20}Cl_2O.4HNO_3 + 2AgCl + 2HNO_3$. A very characteristic reaction of this salt was observed by Hadow; a very dilute solution of platinous chloride strongly acidulated with nitric acid giving with it a beautiful copper-coloured, moss-like precipitate.

Besides these compounds, other platinum bases derived from ammonia have been obtained, of which the following is a brief account:

Platosammonic oxide; Reiset's second base; $Pt''(NH_3)_2O$ or $N_2Pt''H_4.OH_2$.—This is a greyish mass insoluble in water and in ammonia, which may be obtained by heating platosodiammonic hydrate, $Pt''(NH_2.NH_4.OH)_2$ or $N_4Pt''H_{10}.2OH_2$, at 110° (230° F.), as long as it gives off water and ammonia. It combines with acids, and forms salts, most of which are insoluble, and are decomposed on the application of heat. Platosammonic chloride, $Pt''(NH_3)_2Cl_2$ or $N_2Pt''H_4.2HCl$, may be obtained by heating the chloride of platosodiammonium at 250° (482° F.), until it ceases to give off water and ammonia.

Platosemidiammonic compounds, $R.Pt''.NH_2.NH_4R$. — These are isomeric with the platosammonic compounds, $RH_3N.Pt''.NH_3R$. The chloride was obtained by Peyrone, by the action of ammonia on a cold solution of platinous chloride in hydrochloric acid. The yellowish-green product when treated with boiling water leaves a green salt, and the solution on cooling deposits the chloride of the new base in small yellow prisms.

Platosodiammonic hydrate; $Pt''(N_2H_6)_2(OH_2)$.—This substance known as *Reiset's first base*, $N_4Pt''H_{10}.2OH_2$, may be obtained as a hydrate in deliquescent needles, which are powerfully alkaline, caustic, and absorb carbonic anhydride from the air. It is usually isolated by decomposing its sulphate with the equivalent quantity of baric hydrate. In order to prepare its salts, Hadow recommends platinous chloride to be dissolved in warm moderately strong ammonia, filtered from any oxide of iron or iridium, and then concentrated by evaporation; a large crop of crystals of platosodiammonic chloride, $Pt''(N_2H_6)_2Cl_2.OH_2$ or $N_4Pt''H_{10}.2HCl.OH_2$ is deposited on cooling. If a solution of the salt be decomposed with an equivalent quantity of argentic sulphate, platosodiammonic sulphate is formed, and may readily be obtained in crystals; the nitrate may be prepared in a similar way by substituting argentic nitrate for the sulphate. These salts are readily recognized by yielding a precipitate of the green compound of Magnus on the addition of a solution of platinous chloride; this compound being in fact the chloroplatinite of platosodiammonium. Hadow finds that the green compound of Magnus is but one of a series of double salts that platosodiammonic chloride forms with other metallic chlorides, such as mercuric chloride, and the chlorides of cadmium, palladium, tin and copper.

Platinammonic hydrate; $(OH)_2Pt^{iv}(NH_3)_2(OH)_2$.—This compound (*Gerhardt's base*; $N_2Pt^{iv}H_2.4OH_2$) may be obtained in the form of very brilliant striated, rhomboidal prisms of a yellowish colour, by adding ammonia to a boiling solution of the neutral nitrate. It is nearly insoluble in boiling water, is not decomposed by a boiling solution of potassic hydrate, but is readily dissolved by dilute acids, and forms a large number of crystallizable, sparingly soluble salts, which are of a yellowish colour. Some of these salts are neutral, and some are acid. If platosammonic chloride be suspended in boiling water, and a current of chlorine passed through the mixture, it combines with the chlorine, and is slowly transformed into platinammonic chloride, $Cl_2Pt^{iv}(NH_3)_2Cl_2$ or $N_2Pt^{iv}H_2.4HCl$, the reaction being

$Pt''(NH_3)_2Cl_2 + Cl_2 = Cl_2Pt^{iv}(NH_3)_2Cl_2$; by long boiling with argentic nitrate the chloride is converted into basic platinammonic nitrate, $(OH)_2Pt^{iv}(NH_3)_2(NO_3)_2.2OH_2$, or $N_2Pt^{iv}H_2.2HNO_3.4OH_2$.

Platinosemidiammonic chloride, $Cl_3Pt^{iv}NH_2.NH_4Cl$, isomeric with platinammonic chloride (Gerhardt's chloride) is obtained in yellow hexagonal plates on treating platosemidiammonic chloride with chlorine. It becomes olive-green when heated to 160° (320° F.), and dissolves in solution of potassic hydrate with evolution of ammonia.

Platinodiammonic compounds, $R_2Pt^{iv}(NH_2.NH_4.R)_2$.—These include Gros's and Raewsky's salts, in which the electronegative groups, R, united directly with the quadrivalent platinum are not removed by double decomposition. The formation of Gros's chloronitrate has already been described. The chloride, $Cl_2Pt^{iv}(N_2H_6Cl)_2$, may be obtained by passing chlorine into a solution of platosodiammonic chloride.

Diplatosodiammonic hydrate, $(Pt_2)''(NH_2.NH_4.OH)_2$.—This is formed when platosemidiammonic chloride is boiled with a solution of sodic hydrate, as a greyish crystalline powder, which detonates violently when heated. The salts are black, insoluble powders.

The following table contains Blomstrand's general formulæ of the principal series of salts of those compounds which have been ascertained to exist, R representing any univalent negative radicle, as Cl, OH, NO_3, &c.:*

1.—Platosammonium (*Reiset's second base*) ...	$Pt'' \begin{cases} NH_3R \\ NH_3R \end{cases}$
2.—Platosemidiammonium	$Pt'' \begin{cases} NH_2(NH_4)R \\ R \end{cases}$

* The following papers may be consulted upon this subject: Gros, *Ann. Chim. Phys.*, 1863, [2], lxix. 204; Reiset, *ib.*, 1844, [3], xi. 417; Raewsky, *ib.*, 1848, [3], xxii. 278; Peyrone, *Ann. Chem. Pharm.*, li. 1, and lv. 205; Gerhardt, *Comptes Rendus des Travaux de Chimie*, par Laurent et Gerhardt, 1849, p. 113, and 1850, p. 273; Buckton, *Jour. Chem. Soc.*, v. 213, and vii. 22; Hadow, *Jour. Chem. Soc.*, 1866, xix. 345; Blomstrand, *Deut. chem. Ges. Ber.*, 1871, iv. 40; Cleve, *ibid.*, 1873, vi. 1469.

These different bases may also be regarded as ammonias in which part of the hydrogen in one or in two molecules of ammonia has been displaced by *platinosum*, Pt'', or by *platinicum*, Pt^{iv}; platosamine and platinamine being formed upon the type of two molecules of ammonic oxide, N_2H_8O, or $N_2H_6.OH_2$, and diplatosamine and diplatinamine upon that of 4 molecules, $N_4H_{16}O_2$, or $N_4H_{12}.2OH_2$, as will be rendered manifest by examining the formulæ given in the table. Blomstrand, however, as shown above, assigns to them constitutional formulæ, in which the nitrogen atoms are in most cases united by bivalent or quadrivalent platinum, thus the platosammonic chloride is $ClH_2N.Pt''.NH_3Cl$, and platinammonic chloride, $ClH_2N.Pt^{iv}.NH_3Cl$.

3.—Platosomonodiammonium ... ... $Pt''\left\{\begin{matrix}NH_2(NH_4)R\\NH_3R\end{matrix}\right.$

4.—Platosodiammonium (*Reiset's first base*) ... $Pt''\left\{\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\right.$

5.—Platinammonium (*Gerhardt's base*) ... $R_2Pt^{iv}\left\{\begin{matrix}NH_3R\\NH_3R\end{matrix}\right.$

6.—Platinosemidiammonium ... . $R_2Pt^{iv}\left\{\begin{matrix}NH_2(NH_4)R\\R\end{matrix}\right.$

7.—Platinomonodiammonium ... ... $R_2Pt^{iv}\left\{\begin{matrix}NH_2(NH_4)R\\NH_3R\end{matrix}\right.$

8.—Platinodiammonium (*Gros's salts*) ... ... $R_2Pt^{iv}\left\{\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\right.$

9.—Diplatinammonium ... ... $R_2(Pt_2)^{iv}\left\{\begin{matrix}NH_3R\\NH_3R\\NH_3R\\NH_3R\end{matrix}\right.$

10.—Diplatosodiammonium ... ... $(Pt_2)''\left\{\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\right.$

11.—Diplatinodiammonium ... ... $R_4(Pt_2)^{vi}\left\{\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\right.$

12.—Diplatinotetradiammonium ... ... $R_2(Pt_2)^{vi}\left\{\begin{matrix}NH_2(NH_4)R\\NH_2(NH_4)R\\NH_2(NH_4)R\\NH_2(NH_4)R\end{matrix}\right.$

Besides the salts given in the above table, numerous others have been obtained by the action of organic bases on platinous chloride, and on the ammonia bases just noticed.

Fulminating platinum, $N_2Pt^{iv}H_2.4OH_2$?, is procured as an insoluble black powder by dissolving ammonic platinic chloride, $2NH_4Cl.PtCl_4$, in a solution of sodic hydrate and adding an excess of acetic acid, or by precipitating the sulphate with an excess of ammonia. It may be regarded as hydrated diammonic oxide, $(NH_4)_2O.2OH_2$, in which 4 atoms of hydrogen have been displaced by one atom of platinum. Hydrochloric acid dissolves this compound, forming with it a very soluble, uncrystallizable salt: other acids decompose it with formation of ammoniacal salts. If suddenly heated to about 200° (392° F.) it explodes.

(1176) **HYDRIC PLATINIC BROMIDE**; $PtBr_4.2HBr+9OH_2$, may be obtained in transparent, crimson prisms by evaporating a solution of platinum in a mixture of nitric and hydrobromic acids, over quicklime. On heating this at 200° (392° F.) a yellow mass is formed which, when washed with water, leaves platinous bromide, $PtBr_2$, as a greenish-brown powder. Both platinic and platinous bromides form double salts with the alkaline bromides.

(1177) **PLATINIC IODIDE**; PtI_4.—On adding potassic iodide to a dilute solution of platinic chloride the liquid assumes a deep wine-red colour; the mixture remains clear at ordinary temperatures, but becomes turbid and deposits a brown, sparingly soluble powder when heated: this, however, contains excess of iodine. It dissolves in hydriodic acid, forming a dark crimson solution from which *hydric platinic iodide*, $PtI_4.2HI.9OH_2$, may be obtained in large, monoclinic, deliquescent crystals. An *iodochloride of platinum*, PtI_2Cl_2, has also been obtained in large brick-red prisms, which are deliquescent.

(1178) **PLATINOUS OXIDE**, or *Protoxide of platinum*; $PtO = 213{\cdot}1$.—There are three oxides of platinum, a protoxide, PtO, a dioxide, PtO_2, and an intermediate platinosoplatinic oxide, Pt_3O_4. The protoxide may be prepared by digesting platinous chloride in a solution of potassic hydrate; a dark olive-green liquid is thus obtained, owing to the solution of the oxide in the excess of alkali. On neutralizing the solution with sulphuric acid, the black hydrated platinous oxide subsides. It is slowly dissolved by acids, forming unstable salts with them, and is readily decomposed by heat. Platinous sulphite forms several soluble double salts with the sulphites of the alkalies, such as $2(3K_2SO_3.PtSO_3).3OH_2$, obtained by heating potassic platinous chloride with a solution of hydric potassic sulphite, when minute straw-yellow prisms are deposited on cooling. Corresponding ammonium and silver salts exist.

(1179) **PLATINIC OXIDE**, or *Dioxide of platinum*; $PtO_2 = 229{\cdot}1$.—This compound has a strong tendency to combine with alkaline bases; it is therefore prepared by adding to a solution of platinic nitrate only one-half of the quantity of sodic carbonate which is necessary for its complete precipitation. It is thus obtained as a voluminous brown hydrate, $PtO_2.2OH_2$, from which water is expelled at a gentle heat, whilst the mass becomes darker; a higher temperature expels the whole of the oxygen. Hydrated platinic oxide is soluble in solutions of potassic and sodic hydrates, and the compounds thus formed may be obtained in crystals. The sodium compound consists of $Na_2O.3PtO_2.6OH_2$. Platinic oxide also enters into combination with other bases, forming compounds most of which are insoluble. This oxide is also soluble in acids, and forms well characterized salts, the solutions of which have a yellowish-brown colour.

Platinosoplatinic oxide, Pt_3O_4, is obtained by heating 1 part of sodic platinic chloride with 4 of sodic carbonate until the mixture begins to fuse (the potassic salt cannot be substituted

for the sodic salt in this reaction): the residue is exhausted with water, and washed first with dilute nitric acid, then with hot nitric acid, and finally with water. Dried at 110° (230° F.), it forms a black powder which readily loses its oxygen at a red heat, and is reduced by hydrogen at the ordinary temperature.

(1180) **SULPHIDES OF PLATINUM.**—Platinum combines with sulphur in two proportions, PtS and PtS_2.

Platinous sulphide, PtS, may be obtained as a black precipitate by passing sulphuretted hydrogen over moistened platinous chloride; it is also formed by heating sulphur with ammonic platinic chloride, when it assumes the form of a grey powder of metallic appearance, from which the sulphur is completely expelled by heating it in the open air.

Platinic disulphide, PtS_2, is most conveniently prepared by decomposing the sodic platinic chloride by sulphuretted hydrogen; it falls as a dark brown powder, which becomes black during desiccation. It is somewhat soluble in the sulphides of the alkali-metals. By ignition in closed vessels it is converted into proto-sulphide. When exposed to the air, and gently heated, it is partly converted into platinic sulphate, but at a higher temperature is wholly decomposed, metallic platinum remaining.

If precipitated platinic sulphide is thoroughly washed, and after being dried at 100° (212° F.) is exposed to the air for some days, it absorbs oxygen, and a compound, $Pt_2S_2O(OH)_2$, is formed; an intermediate compound, $PtS(OH)_2$, also appears to exist, the reactions being $PtS_2 + 2OH_2 + 2O_2 = PtS(OH)_2 + H_2SO_4$, and $2PtS(OH)_2 = Pt_2S_2O(OH)_2 + OH_2$ (E. Meyer, *Jour. pr. Chem.*, 1878, [2], xvi. 1).

(1181) **PLATONITRITES.**—When potassic platinic chloride is heated with a solution of potassic nitrite, a new salt is formed of the composition $K_2(NO_2)_4Pt$, called *potassic platonitrite*, in which the $(NO_2)_4Pt$ plays the part of a dibasic acid radicle. The platonitrites crystallize well, and many of them are sparingly soluble in water. They may be obtained from baric or argentic platonitrite by double decomposition with the sulphates or chlorides of the respective metals. A large number of these salts have been described by Nilson (*Jour. pr. Chem.*, 1877 [2], xvi. 241).

Platino-iodo-nitrites.—On heating potassic or baric platonitrite with an alcoholic solution of iodine, a powerful action takes place accompanied by evolution of gas and formation of aldehyde, the solution becoming of a bright yellow colour. The product of the reaction is *potassic platino-iodo-nitrite*, $K_2(NO_2)_2I_2Pt.2OH_2$, crystallizing in very large, yellow, four-sided prisms permanent in the air: the baric salt is equally beautiful, and both are readily soluble in water (Nilson, *Deut. chem. Ges. Ber.*, 1877, x. 930).

Diplatonitrites.—On attempting to prepare the platonitrites of glucinum, iron, or indium, nitrous acid is given off and a diplatonitrite of the metal is formed, the general reaction being:

$$2R_2(NO_2)_4Pt = R_2(NO_2)_4Pt_2O + 2RNO_2 + N_2O_3.$$

Some of the platonitrites undergo a similar decomposition when

heated in aqueous solution. The diplatonitrites, like the platonitrites, crystallize well: the silver salt, $Ag_2(NO_2)_4Pt_2O$, forms tufts of minute greenish prisms which are insoluble in water.

Triplatino-octonitrosic Acid.—When a solution of baric platonitrite is decomposed with dilute sulphuric acid, and the filtered liquid evaporated *in vacuo* over sulphuric acid, microscopic needles of a brilliant crimson colour are obtained, which Lang regarded as acid platinous nitrite: Nilson, however (*ibid.*, x. 934), who has recently examined this product, finds that nitrous acid is given off during the evaporation, and that the crystals have the composition of triplatino-octonitrosic acid, $H_4(NO_2)_8Pt_3O.2OH_2$, so that it would appear that the platonitrous acid formed by the decomposition of the baric salt is very unstable, readily giving up nitrous acid, and passing into the new acid. The potassic salt, $K_4(NO_2)_8Pt_3O.2OH_2$, crystallizes in lustrous, chrome-yellow plates, easily soluble in hot water.

(1182) **Other Platinum Compounds.**—*Platinic sulphate* may be formed by dissolving platinic oxide in dilute sulphuric acid, or by treating the disulphide with fuming nitric acid, and heating, to expel the excess of nitric acid. *Platinic nitrate* may be formed by decomposing a solution of the sulphate by an equivalent quantity of baric nitrate; both these platinic salts yield insoluble double basic salts on the addition of an alkali. *Platinous sulphite*, $PtSO_3$, formed by dissolving platinous oxide in aqueous sulphurous acid, forms colourless crystalline double salts with ammonic and potassic sulphites. Powdered platinum and crystallized silicon when heated together in the proper proportions unite to form a *silicide of platinum*, $PtSi_2$. It is a bright crystalline mass of metallic appearance, and very brittle (comp. p. 881).

(1183) **PHOSPHOPLATINIC COMPOUNDS.**—When spongy platinum is heated with phosphoric pentachloride in molecular proportions at 250° (482° F.), a red-brown, crystalline mass is obtained, which may be purified by crystallization from chloroform or benzene. *Monophosphoplatinic chloride*, $PtPCl_5$ or $Cl_2Pt{=}PCl_3$, as thus prepared crystallizes in beautiful maroon-coloured needles which melt at 170° (338° F.), and at a higher temperature is resolved into platinous chloride and phosphorous trichloride. It unites readily with chlorine, forming a *phosphoplatinic perchloride*, $PtCl_3.PCl_4$, as a yellow powder.

When phosphoplatinic chloride is dissolved in water and the solution evaporated in a vacuum, orange-red crystals of *phosphoplatinic acid*, $Cl_2Pt{=}P(OH)_3$, are obtained, which are very deliquescent and soluble. Its salts decompose with great readiness; those of the alkali-metals have not been prepared, as on neutralizing the solution of the free acid it quickly blackens and decomposes. The chloride when treated with alcohols instead of water yields corresponding phosphoplatinic ethers.

Diphosphoplatinic chloride, $Cl_2Pt(PCl_3)_2$, is easily prepared by dissolving the monophosphoplatinic compound in excess of phosphorous trichloride. It forms brilliant yellow crystals which melt at 160° (320° F.), and are soluble in chloroform and benzene. By the action of water, it yields *diphosphoplatinic acid*, $Cl_2Pt{=}P_2(OH)_6$, but great care must be taken to prevent any rise of temperature, as otherwise another acid, $PtClOP_2(OH)_5$, is formed, much more stable than diphosphoplatinic acid. The new acid forms colourless crystals, whilst diphosphoplatinic acid crystallizes in pale yellow needles.

(1184) **Characters of the Salts of Platinum.**—1.—The *platinous salts* are unimportant.

2.—Of the *platinic salts*, the tetrachloride is the only soluble compound of frequent occurrence. These salts are distinguished by the following characters. When heated, they are all decomposed, and leave a residue of metallic platinum. They have a brownish-yellow colour in solution: with *potassic hydrate*, or with any potassic salt, they give a yellow precipitate of potassic platinic chloride, which is soluble in a large excess of the alkali; *sodic hydrate* causes a brown precipitate of hydrated dioxide which is soluble in excess of the alkali; with *ammonia*, or a soluble salt of ammonium, yellow ammonic platinic chloride is precipitated, which is decomposed by heat, leaving metallic platinum. *Sulphuretted hydrogen* and *ammonic hydric sulphide* give a black sulphide which is soluble in a large excess of the sulphides of ammonium and of the alkali-metals.

Solutions of the platinic salts are reduced by *mercurous nitrate*, but not by *ferrous sulphate*. *Stannous chloride* in acid solutions produces a very deep brown solution, but yields no precipitate: *potassic iodide* slowly gives a brown precipitate of platinic iodide, which becomes more abundant when heated. The solutions of the platinic salts are readily reduced to the metallic state by means of *zinc* or *iron*. Oxalic acid exerts no reducing action upon the salts of platinum, which may thus be separated from those of gold; and after the gold has been precipitated in this manner, the platinum may be thrown down in the metallic form by boiling the liquid with a soluble formate, taking care first to neutralize the liquid by the addition of sodic carbonate.

(1185) **Estimation of Platinum.**—Platinum may be estimated either in the metallic state, or in the form of a double chloride of platinum with potassium or ammonium. The solutions from which these double salts are precipitated should be concentrated; the complete separation of the salt is favoured by the addition

of alcohol, and the washing of the precipitate should be performed with dilute alcohol. Platinum may thus be separated from all the metals hitherto described: 100 parts of the potassic platinic chloride contain 40·36 of the metal; and 100 parts of the ammoniacal double salt contain 44·18 of platinum.

§ V. PALLADIUM: Pd″=106·5.

(1186) **PALLADIUM**: *Density* from 11·4 to 11·8; *Fusing-pt.* 1360° (2480° F.); *usually Dyad; rarely Tetrad.*—This is one of the rare metals which occur chiefly in the ore of platinum, in which it was discovered by Wollaston, in the year 1803. It usually forms from a half per cent. to one per cent of these ores. According to G. Rose, palladium is dimorphous, since it is found native in cubes, and in six-sided plates.

In order to extract the metal from the ore of platinum, the solution of this ore in aqua regia is treated with ammonic chloride with a view to separate the platinum, as already described (1167), and to the filtered liquid a solution of mercuric cyanide is added; a yellowish-white, flocculent precipitate of palladious cyanide is produced, which is converted into sulphide by heating it in contact with sulphur, and the sulphur is subsequently expelled by repeated roastings. Another source of this metal is the native alloy of gold and palladium, found in the Brazilian mines. In order to extract the palladium from it, Mr. Cock directs the alloy to be fused with silver, and then boiled in nitric acid, by which all the metals except the gold are brought into solution. The decanted liquid is next mixed with a solution of common salt, by which the whole of the silver is thrown down in the form of chloride, whilst the palladium and the other metals (principally copper with some lead and iron) still remain dissolved. Bars of metallic zinc are then introduced into the liquid, and these metals are precipitated upon the zinc in the form of a black powder. This precipitate is washed and redissolved in nitric acid, supersaturated with ammonia, which dissolves the oxides of palladium and copper, whilst those of iron and lead are precipitated: the clear liquid is now supersaturated by hydrochloric acid. Palladium is thus thrown down in the form of a yellow, sparingly soluble palladamine hydrochloride, $N_2Pd^{iv}H_6Cl_2$; by ignition of this salt the palladium is reduced, and agglutinates, but does not fuse. A small quantity of palladium still remains in solution, and may be recovered by the introduction of bars of iron.

Palladium is a white, hard metal possessed of considerable

ductility and tenacity. It is not fusible in an ordinary wind furnace, but melts at a lower temperature than platinum. Deville and Debray state that, like silver, it absorbs oxygen when melted, and as the metal cools the globule spits. Before the oxyhydrogen blowpipe it burns with scintillation, and if heated on lime it is slowly dispersed in green vapours. It undergoes no change in the open air at ordinary temperatures, but at a low red heat it becomes covered with an iridescent film, owing to superficial oxidation: on increasing the heat, the oxygen is expelled, and the metal recovers its brilliant metallic lustre. Palladium is dissolved when heated with nitric acid or aqua regia, but it is only acted upon with difficulty by the other acids. When fused either with hydric potassic sulphate, with nitre, or with the alkaline hydrates, it is oxidized. If a solution of iodine in alcohol be evaporated on a slip of palladium, a stain is left, by which this metal is at once distinguished from platinum. Palladium combines readily with gold, which is rendered brittle by its presence even in small proportion. It has a remarkable power of whitening the colour of gold, even when present in the mixture in small quantity, and with 20 per cent. of the metal the alloy is quite white. If palladium is alloyed with twice its weight of silver, it forms a ductile compound not liable to tarnish, and well adapted for the construction of small weights. When melted with 8 times its weight of tin, at a red heat, an alloy is formed, Pd_3Sn_2, which is obtained in beautiful, brilliant lamellæ on digesting the mass, when cold, in hydrochloric acid. Palladium has been applied in a few cases to the construction of graduated scales for astronomical instruments, for which, by its whiteness, hardness, and inalterability in the air, it is well adapted. This metal possesses in a remarkable degree the property of absorbing many times its volume of hydrogen, which it gives out again at a high temperature (70 *a*). Troost and Hautefeuille (*Compt. Rend.*, 1873, lxxvii. 686), from a careful study of the tension of palladium saturated with hydrogen, regard it as consisting of the compound, Pd_2H, holding hydrogen in solution.

If a piece of palladium foil or wire be held in the flame of a spirit-lamp, soot is speedily deposited in large quantity, the foil or wire is corroded, and it expands to many times its volume, the mass of soot being found to contain palladium throughout: when the mass of carbon is burnt away a fine skeleton of palladium is left, penetrated by the carbon, and quite brittle.

(1187) **PALLADIOUS CHLORIDE**, or *Chloride of palladium*; $PdCl_2 = 177{\cdot}5$.—This is obtained by evaporating to dryness a solu-

tion of palladium in aqua regia; it forms brown hydrated crystals, which become black when the water is expelled; if heated to redness metallic palladium is left. Palladious chloride forms double salts with the soluble chlorides; those with potassium and ammonium are dark bottle-green. With ammonia, palladious chloride forms a series of compounds analogous to those of platinum (Hugo Müller, *Ann. Chem. Pharm.*, 1853, lxxxvi. 341) (1175): by mixing a moderately concentrated solution of palladious chloride with a slight excess of ammonia a flesh-red precipitate is formed, $N_2PdH_6Cl_2$, which at 100° (212° F.), when moist, passes into a yellow isomeric compound. This latter contains a salt of *palladamine*, N_2PdH_6O, a crystallizable, powerfully alkaline base which forms definite salts with acids.

Palladic Chloride, $PdCl_4$, exists in solution in aqua regia, but cannot be obtained in crystals: it forms double salts with the chlorides of the alkali-metals: the double salt with potassium, $2KCl.PdCl_4$, crystallizes in ruby-red prisms.

(1188) **PALLADIOUS IODIDE**, or *Iodide of palladium*; $PdI_2 = 360{\cdot}5$; *Comp. in* 100 *parts*, Pd, 29·54; I, 70·46.—This compound is obtained by adding a solution of a salt of palladium in slight excess to one of potassic iodide. It is a black powder, insoluble in water, but soluble in ammonia and in a solution of potassic iodide: a solution of palladious nitrate is sometimes employed as a precipitant for iodine when it is necessary to separate iodine from chlorine and bromine (564). Palladious iodide loses its iodine when strongly heated.

(1189) **PALLADIOUS CYANIDE**; $PdCy_2 = 158{\cdot}5$.—Cyanogen has a stronger attraction for palladium than for any other metal, so that a solution of a palladious salt will decompose one of mercuric cyanide. This cyanide is obtained as a yellowish precipitate by adding potassic or mercuric cyanide to neutral solutions of any of the palladious salts; it is soluble in ammonia, in acids, and in potassic cyanide; it forms a series of double cyanides.

(1190) **OXIDES OF PALLADIUM.**—This metal appears to form three oxides; a suboxide, Pd_2O, which furnishes a series of salts resembling those of cuprous oxide, and which, according to Kane, is obtained by heating the hydrated protoxide to incipient redness; a protoxide, PdO, the base of the ordinary salts of the metal; and a dioxide, PdO_2.

The *protoxide, palladious oxide*, $PdO = 122{\cdot}5$, may be obtained as a black powder, by heating the nitrate to low redness; or it may be precipitated by adding potassic or sodic carbonate to a palladious salt, as a dark brown hydrate, soluble both in acids and in alkalies, and from which the water may be expelled by heat. At a bright red heat it loses its oxygen.

The *dioxide, palladic oxide,* $PdO_2 = 138{\cdot}5$, is prepared by decomposing the solid *potassic palladic chloride,* $2KCl.PdCl_4$, by a solution of potassic hydrate; it forms a yellowish-brown hydrate, which obstinately retains a portion of alkali; it is soluble in the alkalies: by boiling it with water, it is rendered anhydrous, and is then deposited as a black powder.

(1191) **SULPHIDES OF PALLADIUM.**—Three of these appear to exist.

Palladious sulphide, $PdS = 138{\cdot}5$, may be formed either directly, by heating powdered sulphur with palladium, or by precipitating a palladious salt by means of sulphuretted hydrogen; it forms a fusible, greyish-white, lustrous mass, from which a portion of the sulphur is expelled by long-continued roasting in a current of air, leaving an oxysulphate of palladium.

Palladic disulphide, PdS_2, is obtained as a dark brown, crystalline powder by fusing the monosulphide with 3 parts of sodic carbonate and 3 of sulphur, exhausting the product with alcohol, and decomposing the residue with dilute hydrochloric acid. It forms double salts with the alkaline sulphides. A *subsulphide,* Pd_2S, has also been obtained.

(1192) **PALLADIOUS SULPHATE,** $PdSO_4$, may be obtained by decomposing the nitrate by sulphuric acid, or by dissolving the oxide in sulphuric acid. It is a deliquescent salt which forms a deep brownish-red solution; when heated it loses acid, and furnishes a basic salt.

On passing a current of sulphurous anhydride through a solution of palladium dichloride it becomes pale yellow, and on adding sodic hydrate a crystalline compound is obtained, consisting of a double *sulphite of palladium and sodium* of the formula, $PdSO_3.3Na_2SO_3.2OH_2$.

(1193) **PALLADIOUS NITRATE** is formed by boiling palladium with nitric acid; it may be obtained in rhombic prisms, which are freely soluble in a small quantity of water, and yield a deep reddish-brown liquid; on largely diluting the solution, the normal salt is decomposed, and an insoluble basic nitrate is precipitated. If ammonia in excess be added to the solution of the nitrate, a crystalline ammoniacal palladious nitrate may be obtained in rectangular tables.

(1194) **Characters of the Salts of Palladium.**—Palladious salts, or the ordinary salts of the metal, yield either brown or red solutions, which when neutral are distinguished by the yellowish precipitate of palladious cyanide, formed on adding *mercuric cyanide.* The *alkaline hydrates* precipitate palladious compounds

in the form of a red or orange basic salt, which is soluble in excess of the alkali by the aid of heat. *Ammonia* and *ammonic carbonate*, when added to a solution of palladious chloride, give a flesh-coloured precipitate soluble in excess of ammonia. Palladious nitrate gives a brown precipitate with ammonia. *Potassic* and *sodic carbonates* yield a brown precipitate of hydrated palladious oxide, with palladious salts. *Potassic iodide* precipitates a black palladious iodide. *Sulphuretted hydrogen* and *ammonic hydric sulphide* throw down a black palladious sulphide insoluble in the sulphides of the alkali-metals. Solutions of the salts of palladium are reduced by a solution of *ferrous sulphate*, and by many of the metals, the reduction being facilitated by heat. *Stannous chloride* produces a dark brown precipitate soluble in hydrochloric acid, and forming an intensely green solution, which becomes reddish-brown on dilution.

Palladium may be separated from all other metals, except copper and lead, by the addition of mercuric cyanide to the solution previously neutralized by means of sodic carbonate. Palladious cyanide when ignited in the air leaves metallic palladium.

§ VI. RHODIUM: $Ro''' = 104{\cdot}3$.

(1195) **RHODIUM**: *Density*, 12·1.—This metal was discovered by Wollaston in 1803: it usually forms about one-half per cent. of the ore of platinum, and may be extracted from the solution of this ore in aqua regia, after the platinum and palladium have been separated by the addition of ammonic chloride and mercuric cyanide; the excess of the cyanide is decomposed by acidulating the solution with hydrochloric acid, adding common salt, and evaporating to dryness; the sodic chloride then forms double chlorides with all the metals in solution; the residue is treated with alcohol of density 0·837, which dissolves all these double salts, except that of sodium and rhodium, which remains behind as a red powder; this is dissolved in water, and the rhodium thrown down in a pulverulent form by means of bars of metallic zinc. The sodic rhodic chloride may also be decomposed by heating it in a current of hydrogen gas, when, on washing the mass with water, the rhodium is left in a pulverulent form.

Rhodium is a white, very hard metal; when quite pure, it is malleable after fusion upon lime, and it then has a density of 12·1. It requires a stronger heat to fuse it than platinum, and when melted has a similar tendency to absorb oxygen, and to spit as the globule sets.

Deville says that rhodium furnishes an alloy with platinum, which is easily worked; when the proportion of rhodium forms 30 per cent. or upwards of the alloy, it is not attacked by aqua regia. When pure, rhodium is insoluble in the acids, although if alloyed in small quantity with platinum, copper, bismuth, or lead, it is dissolved with them in nitro-hydrochloric acid. Rhodium has a considerable attraction for oxygen, and becomes oxidized when heated to redness, or by fusion with a mixture of nitre and potassic carbonate; hydric potassic sulphate also oxidizes the metal and forms a soluble potassic rhodic sulphate, $KRo2SO_4$, whilst sulphurous anhydride escapes. If heated in contact with sodic chloride, in a current of chlorine, a soluble sodic rhodic chloride, $3NaCl.RoCl_3$, is produced.

(1196) **CHLORIDES OF RHODIUM.**—Three of these, viz., $RoCl_2$; Ro_2Cl_5; and $RoCl_3$, were stated by Berzelius to exist, but according to Claus there is but one definite compound of rhodium and chlorine.

Rhodic chloride, $RoCl_3$, formerly called the *sesquichloride*, is obtained in the anhydrous state by igniting the finely-divided metal in a current of chlorine; as thus prepared it is insoluble, but by decomposing the potassic rhodic chloride by silicofluoric acid, and separating the potassic silicofluoride by filtration, a solution is obtained, which on evaporation yields a red-brown mass of the hydrate, $RoCl_3.4OH_2$. This chloride unites with many of the soluble chlorides to form crystallizable double salts, which are of a ruby or rose colour, whence the metal receives its name (from ῥόδον, a rose); the sodium salt, $3NaCl.RoCl_3.12OH_2$, crystallizes in rhombohedra isomorphous with the corresponding iridium salt (p. 906); they are efflorescent in the air, and insoluble in alcohol. When rhodic chloride is supersaturated with ammonia, the precipitate which first forms is redissolved, and on boiling, a characteristic yellow compound, $Ro_2Cl_6.10NH_3$, is produced, which may be purified by evaporation and re-crystallization: when ignited it leaves pure rhodium in the form of a powder. The ammonia compound when treated with argentic oxide yields the corresponding oxide, $R_2O_3.10NH_3$, which is a strong basyl, and forms crystalline salts.

(1197) **OXIDES OF RHODIUM.**—Rhodium has a considerable attraction for oxygen; it appears to form four definite oxides, RoO, Ro_2O_3, RoO_2, and RoO_3.

The *protoxide*, RoO, is formed when the hydrated sesquioxide, $R_2O_3.3OH_2$, is heated to redness in a platinum crucible. It

becomes incandescent, and is converted into the dark grey protoxide, which is quite indifferent to acids.

Rhodic oxide, or *Sesquioxide of rhodium*; $Ro_2O_3 = 256{\cdot}6$.—This is the only salifiable oxide of rhodium; it may be obtained by heating rhodium with a mixture of nitre and potassic carbonate; the oxide forms an insoluble compound with potassic hydrate, which is to be well washed, and decomposed by digestion with hydrochloric acid: the sesquioxide is thus left as a greenish-grey hydrate, $Ro_2O_3.3OH_2$, which is insoluble in all acids. Another hydrate, $Ro_2O_3.5OH_2$, of a yellow colour is formed on treating sodic rhodic chloride with an aqueous solution of potassic hydrate. When this is suspended in a solution of potassic hydrate, and a current of chlorine passed into the liquid, it becomes gradually converted into a green-coloured hydrate of the *dioxide*, RoO_2. The alkaline solution at the same time acquires a deep violet colour, and on being allowed to stand deposits the *trioxide*, RoO_3, as a blue powder.

(1198) **SULPHIDES OF RHODIUM.**—Rhodium forms two sulphides, RoS and Ro_2S_3.

If the metal be heated in the vapour of sulphur, the two bodies unite with incandescence, and form the *protosulphide*, which has a bluish-grey colour, and fuses at a very high temperature; the sulphur burns off in the open air, and leaves a forgeable mass of metallic rhodium. The *sesquisulphide* may be obtained in the form of a brown hydrate by decomposing a hot solution of sodic rhodic chloride by means of potassic or sodic sulphide. A *rhodic sulphate*, $Ro_23SO_4.12OH_2$, may be obtained as a yellowish-white, crystalline mass on oxidizing the sulphide by means of nitric acid.

(1199) **Characters of the Salts of Rhodium.**—The sodic rhodic chloride is the best known of these compounds. The rhodic salts generally form rose-coloured solutions; they are decomposed by *iron* or *zinc*, which causes a deposit of metallic rhodium. *Potassic* and *sodic hydrates* gradually produce a precipitate of yellow hydrated rhodic oxide, which obstinately retains a portion of the alkali; it is soluble in excess of alkali as well as in acids; if alcohol be added to the alkaline solution, a black precipitate is gradually formed without the application of heat. *Potassic iodide* throws down a sparingly soluble yellow triiodide of rhodium. *Sulphuretted hydrogen*, when the solution is heated, slowly forms a brown precipitate insoluble in the alkaline sulphides. The *soluble sulphites* give a pale yellow precipitate.

If the salts of rhodium be heated in a current of hydrogen, the metal is readily reduced: in this form it is insoluble in aqua regia, but if it be fused with hydric potassic sulphate, a double salt is formed which is soluble in water, with a pink colour.

§ VII. RUTHENIUM: Ru = 104·2.

(1200) **RUTHENIUM**: *Density*, 12·261.—This metal which, in 1845, was shown by Claus to exist in the ore of platinum, is very hard and brittle, and is only fusible with difficulty even before the oxyhydrogen blowpipe. The melted metal, according to Deville and Debray, has a density of from 11 to 11·4. It absorbs oxygen at a red heat, and the oxide so obtained is not decomposed by simple elevation of temperature. The metal is readily oxidized by fusion with nitre, or with potassic hydrate. Ruthenium accompanies the alloy of osmium and iridium in a proportion varying from 3 to 6 per cent.; but it is not found in that portion of the platinum ore which is soluble in aqua regia. The metal is most easily obtained from the dioxide by heating it in a current of hydrogen, the oxide is reduced, and the metal is obtained in the form of a dark grey powder. When the metal is fused with five or six times its weight of tin, and the product boiled with hydrochloric acid, a crystalline alloy, $RuSn_2$, is left in the form of regular cubes: heated in a current of dry hydrochloric acid gas, this yields pure ruthenium in the crystalline state.

(1201) **Extraction of Ruthenium.**—This metal is obtained from the residue of the platinum ore after it has been exhausted with aqua regia: this residue frequently contains both titaniferous iron and chrome iron, but its most important constituent is an alloy in flat plates or scales of a white colour and metallic lustre. This was formerly considered to be an alloy of osmium and iridium: it has, however, been found to consist of four metals, viz., osmium, iridium, ruthenium, and a small quantity of rhodium.

Fremy, in separating the different metals contained in this residue, avails himself of the readiness with which the osmium is oxidized, and the volatility of the tetroxide produced. His process is the following:—About 200 grams of the platinum residue placed in a porcelain or platinum tube, and heated to redness, is roasted in a current of dry air; in the portion of the tube which projects from the furnace some fragments of porcelain are placed, and the tube is connected with a series of glass flasks for the

purpose of condensing the tetroxide of osmium as it distils; in the last flask a solution of potassic hydrate is placed in order to retain such portions of the tetroxide as may have escaped condensation, this flask being connected with an aspirator, by means of which a current of atmospheric air is drawn through the apparatus. The air is dried, and freed from organic particles before it enters the heated tube, by causing it to pass through tubes filled with pumice moistened with sulphuric acid. During the operation, the osmium and ruthenium become oxidized; the tetroxide of osmium condenses in beautiful needles in the flasks, and mechanically carries forward the dioxide of ruthenium, which is deposited upon the fragments of porcelain in regular square prisms.*

The fixed residue consists of an alloy of iridium and rhodium, mixed with a little osmium and ruthenium. This is to be fused with potassic hydrate, by which the oxide of ruthenium is removed, and may be dissolved out on washing the fused mass with water. The undissolved portion is ignited with four times its weight of nitre, and the product is treated with boiling water, which dissolves the osmium, and on cooling often deposits it in octahedral crystals as dipotassic osmite, $K_2OsO_4.2OH_2$. The residue now contains only iridic and rhodic sesquioxides in combination with potassium. Aqua regia, when boiled with it, converts most of the iridium into the soluble tetrachloride, and the addition of a solution of potassic chloride to the liquid causes the formation of potassic iridic chloride, $2KCl.IrCl_4$, which is deposited in crystals as the solution cools. The rhodic oxide, which is left undissolved, since it is insoluble in aqua regia, is converted into a soluble double salt by mixing it intimately with an equal weight of sodic chloride, and heating the mass to dull redness in a current of dry chlorine.

(1202) **CHLORIDES OF RUTHENIUM.**—There are three chlorides of ruthenium, $RuCl_2$; $RuCl_3$; and $RuCl_4$.

The *dichloride*, $RuCl_2$, is formed along with the trichloride when metallic ruthenium is heated in a current of dry chlorine, and remains as a black crystalline powder whilst the trichloride sublimes. It is insoluble in water and in acids.

The *trichloride* is also obtained by dissolving the sesquioxide in

* Sometimes the osmide of iridium does not readily undergo oxidation. In such a case Deville fuses it with 8 or 10 times its weight of zinc, and heats it for some hours to full redness; he then dissolves out the zinc by hydrochloric acid, which leaves the platinum metals in the form of a fine black powder which is very easily oxidized in a current of air.

hydrochloric acid; on evaporation it yields a yellowish-brown, crystalline, deliquescent mass, which is soluble in alcohol: it forms slightly soluble double salts with potassic and ammonic chlorides, and also ammoniacal basic compounds similar to those obtained with the other platinum metals. Sulphuretted hydrogen causes a brown precipitate of ruthenic sesquisulphide in solutions of the trichloride, leaving the supernatant liquid of a fine blue colour, probably owing to the formation of a lower chloride of the metal; this reaction, which is very delicate, is characteristic of ruthenium. Metallic *zinc* also reduces the yellow trichloride to the blue dichloride, and ultimately precipitates the metal as a black powder.

The *tetrachloride*, $RuCl_4$, is only known in combination with alkaline chlorides, forming double salts. The potassic salt, $2KCl.RuCl_4$, is brown and very soluble in water: it may be obtained by evaporating a solution of potassic chloride and ruthenic hydrate, $RuO_2.2OH_2$, in hydrochloric acid.

(1203) **OXIDES OF RUTHENIUM.**—Ruthenium forms five compounds with oxygen, RuO; Ru_2O_3; RuO_2; RuO_3; and RuO_4.

Ruthenic anhydride, or *Ruthenic acid*, RuO_3, is insoluble in water: it may be obtained by heating any of the preceding oxides with nitre; dipotassic rutheniate is formed, which is soluble in water with an orange-yellow colour. On passing chlorine into this solution, at a certain stage it becomes deep green, and the liquid is filled with minute black crystals, orthorhombic octahedra isomorphous with potassic permanganate; these are the potassic salt of a new acid, and have the formula, $KRuO_4$. The *sesquioxide*, the most stable of the basic oxides of the metal, is obtained in the anhydrous form by igniting the metal in a current of air. It has a deep blue colour, and is insoluble in acids. The alkalies precipitate the hydrated oxide, $Ru_2O_3.3OH_2$, from a solution of the trichloride as a bulky, blackish-brown powder, which forms soluble salts with acids. The volatile *tetroxide*, RuO_4, analogous to osmic tetroxide, is prepared by fusing 3 parts of ruthenium with 24 of potassic hydrate and 8 of nitre, dissolving the product in water, and passing chlorine into the heated liquid, when it volatilizes as a golden-yellow, crystalline mass which melts at 58° (136°·4 F.), and boils at about 100° (212° F.); it decomposes, however, with the greatest readiness, giving rise to explosion (at 108°) with rapid evolution of gas on attempting to distil it (Deville and Debray, *Compt. Rend.*, 1875, lxxx. 457). It does not appear to be poisonous, differing in this respect from osmic tetroxide, which is very deleterious.

(1204) **Characters of the Compounds of Ruthenium.**—The solutions of the salts corresponding to the sesquioxide form with *plumbic acetate* a characteristic purplish-red precipitate. *Mercuric cyanide* renders the solution blue, whilst a blue precipitate is formed. The *alkaline hydrates* and *carbonates* yield a black precipitate of the sesquioxide, insoluble in excess of the precipitant. The most delicate and characteristic reaction of ruthenium, however, is that with *sulphuretted hydrogen* previously mentioned (p. 900). *Sodic formate* or *oxalate,* if boiled with salts of ruthenium, renders the solution colourless, but does not occasion any precipitate of reduced metal.

§ VIII. OSMIUM: Os=199.

(1205) **OSMIUM**: *Density,* 22·48.—This metal occurs associated with platinum in the form of an alloy of osmium, iridium, and ruthenium. It was discovered in the ore of platinum by Tennant, in 1803. Osmium may be obtained in the metallic condition by several processes. One of the simplest consists in treating volatile oxide of osmium, OsO_4, obtained by Fremy's method (1201) with hydrochloric acid and metallic mercury in a closed vessel at 140° (284° F.). Calomel is thus produced by the decomposition of mercurous oxide, which is formed at the expense of the oxygen contained in the oxide of osmium; $OsO_4+8Hg+8HCl=Os+4Hg_2Cl_2+4OH_2$. The water and the superfluous acid are expelled by evaporation to dryness, and on heating the residue in a small porcelain retort, the excess of mercury and calomel is driven off, leaving pure osmium in a pulverulent form. It may be obtained, according to Deville and Debray (*Compt. Rend.,* 1876, lxxxii. 1076), as a beautiful blue metal with a tinge of grey, by passing osmic tetroxide, in a current of nitrogen, over the pure carbon which is deposited when benzene vapour is passed through a porcelain tube at a high temperature: sometimes in this operation beautiful copper-coloured scales of *sesquioxide of osmium* are obtained which are permanent in the air. In the finely-divided state, the metal emits the odour of tetroxide of osmium, when exposed to a moist atmosphere; it takes fire when heated in the open air, and is dissolved by strong nitric acid, or by aqua regia, being converted into tetroxide of osmium. After ignition, however, it is no longer soluble in the acids. The density of osmium in the pulverulent form is about 10, but after it has been heated to the fusing-point of rhodium in the oxyhydrogen jet, it acquires a density of 21·4, and in the

crystalline state it is 22·477. In order to obtain compact osmium, Deville and Debray oxidize the alloy of osmium and iridium by mixing it intimately with 5½ times its weight of baric dioxide, and heating it to a bright red for 2 hours, after which they distil with a mixture of eight parts of hydrochloric and one of nitric acid. The tetroxide of osmium which passes over is received in a solution of ammonia, supersaturated with sulphuretted hydrogen, and boiled. The tetrasulphide of osmium is separated by filtration, dried at a low temperature, placed in a crucible of gas-coke, which is inclosed in a clay crucible and luted down, then exposed for four or five hours to a heat sufficient to melt nickel. The osmium is reduced, and furnishes a brittle mass, the colour of which has more of a bluish cast than that of zinc. At a still higher temperature in the oxyhydrogen jet, at the fusing-point of rhodium, it becomes still denser. It may be heated in this condition to the fusing-point of zinc without emitting vapour, but it takes fire at a higher temperature. If heated with 7 or 8 times its weight of tin in a charcoal crucible to a full red heat, the osmium is dissolved by the tin, and crystallizes out on slow cooling. On treating the mass with hydrochloric acid, the osmium is left as a very hard crystalline powder. It may also be combined with zinc, and on dissolving the zinc in hydrochloric acid the osmium is left as an amorphous combustible powder. Osmium appears to be the least fusible of the metals. In the oxyhydrogen jet platinum melts and is volatilized, and iridium and ruthenium undergo fusion, but osmium does not melt, although it is volatilized by the intense heat.

Osmium differs remarkably from the other metals of this group, except ruthenium, and presents more analogy with arsenicum and antimony than with the noble metals.

(1206) **CHLORIDES OF OSMIUM.**—There are three chlorides of osmium, viz.—$OsCl_2$; $OsCl_3$; $OsCl_4$: the *osmious dichloride*, $OsCl_2$, formerly the *protochloride*, is of a blue-black colour, and dissolves in water with a dark violet-blue colour; it is produced by heating powdered osmium in a current of chlorine; the double salts which it forms are of a green colour. The *osmic tetrachloride*, $OsCl_4$, formerly the *bichloride*, is formed in the same way as osmious dichloride, employing an excess of chlorine; it is more volatile, and condenses as a red, crystalline, fusible, deliquescent powder: both this and the preceding chloride are soluble in water, which soon decomposes them, forming tetroxide of osmium and hydrochloric acid, and depositing black osmic dioxide. Osmic tetrachloride forms with potassic chloride, octahedral crystals of

a beautiful, sparingly soluble, red salt, $2KCl.OsCl_4$; this is obtained by heating a mixture of osmium and potassic chloride in a current of chlorine: it is isomorphous with the corresponding platinum salt, and yields a characteristic dark olive-green precipitate with argentic nitrate, $2AgCl.OsCl_4$ (Claus). Mercurous nitrate gives with it a reddish-brown precipitate: tannic acid gives with it, when heated, a dark blue solution, and potassic ferrocyanide, a chrome-green liquid, passing into dark blue.

Double salts may also be formed which contain osmious trichloride, $OsCl_3$.

When osmic tetroxide is treated with excess of ammonia, a compound, $N_2H_6OsO_2.OH_2$, is obtained as a brown-black powder, and if potassic hydrate be present, *potassic osmiamate*, $N_2K_2Os_2O_5$, is formed, a yellow, crystalline compound, which detonates readily when struck or suddenly heated.

(1207) **OXIDES OF OSMIUM.**—Five oxides of osmium are known:—OsO; Os_2O_3; OsO_2; OsO_3; OsO_4. The anhydrous *protoxide* of osmium is of a grey-black colour, and insoluble in acids: its bluish-black hydrate is soluble in hydrochloric acid, forming a deep indigo-blue solution of the dichloride, $OsCl_2$, which absorbs oxygen rapidly, and becomes converted into the tetrachloride, $OsCl_4$. The *sesquioxide* is sometimes formed on passing osmic tetroxide in a current of nitrogen over carbon (p. 901); it forms rose-red, uncrystallizable salts. The *dioxide*, OsO_2, is black, and may be obtained by heating potassic osmic chloride, $2KCl.OsCl_4$, with sodic carbonate in a current of carbonic anhydride and exhausting the residue with water. *Osmic hydrate*, $OsO_2.2OH_2$, is formed on adding dilute nitric acid to a solution of potassic osmite, K_2OsO_4. The *trioxide* possesses a feebly acid character; it cannot be isolated, but it forms a violet-coloured, crystalline, sparingly soluble compound with potassium, the *dipotassic osmite*, $K_2OsO_4.2OH_2$; this is a good source of pure osmium. It is easily prepared by adding a little alcohol to a solution of the tetroxide of osmium in potassic hydrate; the osmite then separates as a rose-coloured, crystalline powder, which is permanent in dry air, but absorbs oxygen if moist. If this salt be digested in a solution of ammonic chloride, a yellow, sparingly soluble salt is formed, $2NH_4Cl.N_2OsH_4O_2$, which, when ignited in a current of hydrogen, leaves pure osmium.

Osmic Tetroxide, or *Tetroxide of osmium; Osmic acid;* $OsO_4 = 263$; *Mol. vol.* [ ]; *Rel. wt.* 131·5; *Density of vapour, theoretic,* 9·1; *observed,* 8·88.—This is the volatile compound which is produced when the metal is heated with nitre, or when roasted in

the air: it forms colourless, acicular, transparent, flexible crystals which are readily fusible, and are freely soluble in water; it boils at about 100° (212° F.), emitting an extremely irritating and poisonous vapour, with a pungent, characteristic odour somewhat resembling that of chlorine; hence the name of the metal osmium (from ὀσμή, odour): this oxide does not combine with acids, and although it unites with the alkalies, its solution does not redden litmus; its solutions in the alkalies give off the tetroxide when boiled. It produces a permanent black stain upon the skin, owing to the partial reduction of the metal, and gives a characteristic blue precipitate when its solutions are mixed with tincture of galls. According to Fremy, another oxide of osmium (OsO_5?) exists, but it is very unstable; it forms compounds with potassium and sodium which have a dark brown colour; they sometimes crystallize from concentrated alkaline solutions.

(1208) **SULPHIDES OF OSMIUM.**—If the aqueous solution of tetroxide of osmium, acidulated with hydrochloric acid, be treated with sulphuretted hydrogen, there is an immediate precipitation of the black hydrated *tetrasulphide*, which is slightly soluble in solutions of the sulphides of the alkali-metals. Four inferior degrees of sulphuration of osmium also exist; they correspond in composition with the oxides. These sulphides are decomposed by prolonged ignition, and pure osmium is left.

(1209) **Characters of Osmium Compounds.**—The properties of the salts of osmium have been but incompletely ascertained. When boiled with nitric acid they all evolve vapours of tetroxide of osmium.

§ IX. IRIDIUM: Ir = 198.

(1210) **IRIDIUM**: *Density*, 22·4.—This metal was discovered at the same time as osmium, by Smithson Tennant. It is occasionally found native and nearly pure in considerable masses among the Uralian ores of platinum, but it usually occurs combined with osmium as an alloy in flat scales. Iridium appears to be dimorphous, for it is found crystallized both in cubes and in double six-sided pyramids (G. Rose). In order to obtain the metal in the separate state, Wöhler recommends the powdered alloy to be intimately mixed with an equal weight of finely powdered fused sodic chloride, and the mixture to be heated to dull redness in a glass tube through which a current of dry chlorine is passed as long as it is absorbed. The alloy is decomposed by the chlorine, double chlorides of iridium and sodium,

and of osmium and sodium being formed; these are dissolved in boiling water, and are thus freed from the insoluble portions. This solution is then concentrated, mixed with nitric acid and distilled; the double salt of osmium is decomposed by this means, and the volatile tetroxide of osmium thus formed, passes over with the vapour of water leaving the iridium salt. The addition of ammonic chloride to the concentrated solution in the retort produces a precipitate of the ammonic iridic chloride, which when ignited, yields metallic iridium in a spongy state. The metal, however, if obtained thus, is liable to be contaminated with ruthenium. It is preferable to adopt Fremy's method of preparing the potassic iridic chloride (1201). The salt may be decomposed by ignition in a current of hydrogen; and after the removal of the potassic chloride by washing with water, the iridium is left in the form of a finely-divided powder. In this state, however, it is not pure, and a long and tedious process is necessary to free it from the other platinum metals which obstinately adhere to it (comp. Deville and Debray, *Compt. Rend.*, 1875, lxxxi. 839).

Iridium is a very hard, white, brittle metal, which may be melted on lime by the oxyhydrogen blowpipe, or by the heat of the voltaic current. After having been fused it has a density of 22·4 (Deville and Debray, *loc. cit.*); and a native alloy of platinum and iridium is known which has a density of 22·6. If heated in a finely-divided state in the open air it absorbs oxygen, but if in mass it remains unchanged by exposure to heat. In its isolated form it is unacted on by any of the acids or by aqua regia; but when alloyed with platinum it is readily dissolved by the latter. Pulverulent iridium, when fused with nitre or with the hydrated alkalies, becomes oxidized, and a similar effect is produced by heating it with hydric potassic sulphate. Iridium may be obtained in a finely-divided state by decomposing a solution of its sulphate by alcohol: in this form it is a black powder, which possesses properties similar to those of platinum black (1170).

(1211) **CHLORIDES OF IRIDIUM.**—There are three chlorides of iridium. They all form double salts with the chlorides of the alkali-metals. According to Claus, the *dichloride*, $IrCl_2$ (formerly called the *protochloride*), may be obtained in solution in combination with potassic chloride, if the double salt of trichloride of iridium with chloride of potassium, $3KCl.IrCl_3.3OH_2$, be treated with a solution of hydric potassic sulphite, until the green colour has passed into red; on evaporating the solution carefully, red crystals of the double salt, $4KCl.IrCl_2.2K_2SO_3.IrSO_3.12OH_2$, are deposited.

The *trichloride*, $IrCl_3$ (the old *sesquichloride*), which is the most stable of the three chlorides, is obtained as a black sublimate on heating iridium in a current of chlorine; it is deliquescent and dissolves in water forming a solution of an olive-green colour. Like platinum and palladium, it forms double chlorides with the chlorides of many of the metals; the sodic salt, $3NaCl.IrCl_3.12OH_2$, forms large, well-defined rhombohedral crystals of a deep brown-red colour, isomorphous with the analogous palladium compound (p. 896). It forms a similar salt with potassic chloride. A solution of iridium trichloride gives, with mercurous nitrate, a bright ochre-yellow precipitate, $2IrCl_3.3Hg_2Cl_2$, and a similar compound is formed with argentic nitrate which at first is dark blue, but soon becomes colourless.

The *tetrachloride*, $IrCl_4$, is obtained as a black, deliquescent, amorphous mass on dissolving iridium or any of its oxides in aqua regia and evaporating the solution. If dry chlorine be passed over a mixture of finely-divided iridium and potassic chloride, a potassic iridic chloride, $2KCl.IrCl_4$ (*density* 3·546), of a reddish-black colour, is formed. It dissolves in boiling water, and is deposited in anhydrous octahedra on evaporating the solution; it corresponds in composition to the yellow platinum salt, with which it is isomorphous. A similar salt of sodium may be formed in the same manner, by substituting sodic for potassic chloride: it is freely soluble. Iridic tetrachloride forms a similar salt with ammonic chloride, which possesses a very intense colouring power, and produces a dull brown solution even when much diluted. It is remarkable that the addition of potassic hydrate in small quantity to the tetrachloride, converts it into the olive-green trichloride. Iridic tetrachloride, when heated with ammonia, forms a series of compound bases analogous to those furnished by platinum and palladium.

An *iridic tribromide*, $IrBr_3.4OH_2$, has been obtained in olive-green crystals, and also three compounds with iodine, IrI_2; IrI_3; and IrI_4.

Claus considers that the compounds formerly described as containing trioxide and trichloride (hexachloride) of iridium were really compounds of ruthenium.

(1212) **OXIDES OF IRIDIUM.**—This metal forms four distinct combinations with oxygen, IrO; Ir_2O_3; and IrO_2, corresponding to the chlorides and a higher oxide, IrO_3: they pass readily one into the other, and thus give rise to the variety of tints which solutions of the salts of this metal assume. From

these changes of colour the name iridium, derived from *Iris*, the rainbow, was conferred on the metal.

The *protoxide* is obtained as a black anhydrous powder by decomposing dry iridious dichloride, $IrCl_2$, by means of a concentrated solution of potassic hydrate. It is attacked by acids with difficulty, but is dissolved by the alkaline hydrates; the solution in potassic hydrate absorbs oxygen from the air, and becomes blue. Its solutions in the acids have a dingy green colour.

The *sesquioxide* is the compound formed when potassic iridic chloride, $3KCl.IrCl_3$, is ignited with sodic carbonate in an atmosphere of carbonic anhydride; on exhausting the product with water the sesquioxide is left as a bluish-black powder, which is decomposed by a full red heat, and is readily reduced by hydrogen and by combustible substances. This anhydrous oxide is insoluble in acids, and even in fused hydric potassic sulphate. If a solution of iridic trichloride be boiled with a solution of potassic hydrate, oxygen is absorbed, and an indigo-blue precipitate, which is a hydrated *iridious dioxide*, $IrO_2.2OH_2$, is formed (Claus). It may be rendered anhydrous by a gentle heat. The dioxide is but slowly dissolved by acids; the hydrochloric solution is at first blue, it then becomes green, and, when heated, changes to reddish-brown, whilst iridic tetrachloride is formed.

The *trioxide*, IrO_3, is unknown in the free state, but when iridium is fused for some time with potassic nitrate a *potassic periridate* is formed. On treating the mass with water a basic periridate dissolves, whilst an acid salt is left as a black crystalline powder.

Three *sulphides* of iridium corresponding to the oxides may be prepared by decomposing the chlorides of the metal by means of sulphuretted hydrogen.

Iridium, like palladium, when held in the flame of a spirit-lamp, becomes covered with carbonaceous excrescences, which contain a considerable portion of metallic iridium.

The salts of iridium have been but incompletely examined.

Iridium is apt to accompany the double chlorides of platinum with potassium and ammonium. It may be separated from platinum by precipitating the two metals together, by means of potassic chloride: the precipitate is washed, and either digested with potassic cyanide which dissolves the iridium and leaves the platinum; or it may be fused with twice its weight of potassic carbonate, which reduces the platinum to the metallic state,

whilst the iridium remains in the form of sesquioxide. The potassium salts are removed by washing, and the platinum is redissolved by means of aqua regia, which does not attack the iridic sesquioxide. This operation sometimes requires repetition, as a portion of iridium may escape oxidation on the first occasion.

§ X. DAVYUM.

(1213) **DAVYUM.**—Sergius Kern has recently obtained a minute quantity of a silvery-white metal from the residues left after the separation of rhodium and iridium by Bunsen's method, but scarcely any of its properties are known. The density of the ingot of metal obtained, which weighed only 0·27 gram, was 9·389. It is very difficultly fusible. Its atomic weight is said to be about 154.

The chloride, which is very soluble in water, yields double salts with the chlorides of potassium, sodium, and ammonium: the sodic salt differs from those obtained with other members of the platinum group of metals in being nearly insoluble in water. The sulphate obtained by boiling the metal with sulphuric acid is a yellowish-red salt almost insoluble in water.

CHAPTER XXV.

ON SOME CIRCUMSTANCES WHICH MODIFY THE OPERATIONS OF CHEMICAL ATTRACTION.

(1214) **Modification of Chemical Attraction.**—In the first volume of this work an outline was given of the leading characters of the most important varieties of molecular and polar forces, as viewed in their simplest conditions. In the second volume the attention of the reader has been hitherto principally directed to the results produced by the exertion of chemical attraction in the formation of the various compounds of inorganic origin, without reference to the effects of other forces which may have concurred in their production. It will, however, now be advisable to trace the influence exerted upon the operation of chemical attraction by the co-operation or antagonism of volatility and cohesion, of adhesion, and of heat.

§ I. INFLUENCE OF COHESION, ADHESION, AND VOLATILITY.

(1215) **Influence of Cohesion on Chemical Attraction.**—Since chemical attraction is a force which is exerted only when the particles of bodies are within indefinitely small distances, minute subdivision might be expected to favour its manifestation, by increasing the surfaces, and facilitating the mutual contact of the combining bodies. It will therefore be needless to give more than one or two instances in proof of this point: Iron, copper, lead, and many other metals, in mass, are very slowly acted upon by the air, but if they be reduced to a finely-divided state, they are oxidized with such rapidity as often to become incandescent. When oxide of iron, cobalt, or nickel is reduced by hydrogen at a low red heat, the metal is obtained in this form, and by the interposition of some infusible matter between the particles, as when a little alumina or magnesia is precipitated along with the oxide, the tendency to rapid oxidation in the reduced metal is much increased. Copper, when precipitated from its solutions by metallic iron, or when reduced by means of hydrogen from its oxide at a low temperature, readily ignites and glows like tinder. If a portion of plumbic tartrate be exposed in a glass tube to a heat sufficient to char the acid, the metallic lead is reduced throughout the mass in a state of extreme division, and when poured into the air it generally takes fire, and burns with scintillations.

The opposite influence, exercised by the force of cohesion, is seen on contrasting the facility with which disintegrated carbon burns when in the shape of tinder, with the difficulty which is experienced in effecting the combustion of the compact coke which is deposited from coal-gas upon the interior of the iron retorts; and a decrease of combustibility may be traced through all the different forms of carbon, in proportion as their hardness and density increase.

(1216) **Influence of Adhesion and Solution on Chemical Attraction.**—It is mainly to the intimate subdivision effected by means of solution, that this operation owes its important influence in facilitating chemical combination. Besides this, the freedom with which the molecules of liquids move quickly brings the dissolved bodies in contact with one another.

The influence of solution in favouring chemical action is well exemplified by the effect of nitric acid upon baric carbonate. Baric nitrate, although soluble in water and in dilute nitric acid,

is not soluble in the concentrated acid; when, therefore, concentrated nitric acid is poured upon finely powdered baric carbonate, it only occasions a slight effervescence, although the acid may be in large excess. If the liquid be diluted with a small quantity of water, a brisk effervescence is temporarily renewed, but soon ceases; on a further addition of water, a fresh effervescence occurs, and when the acid has been diluted with 8 or 10 times its bulk of water, the whole of the baric carbonate is decomposed and dissolved.

For a similar reason, alcoholic solutions of acids are without action on the carbonates, unless the resulting salt be soluble in alcohol; thus, a mixture of tartaric acid and alcohol will not decompose potassic carbonate. An alcoholic solution of hydrochloric acid will not decompose potassic carbonate, but will decompose calcic carbonate. An alcoholic solution of nitric acid decomposes calcic but not potassic carbonate. The tartrates are insoluble in alcohol, so are potassic chloride and nitrate, but calcic chloride and nitrate are freely soluble.

(1217) **Influence of Volatility.**—In the numerous instances in which two salts produce mutual decomposition, frequent examples are afforded of the results produced by the interference of other forces with that of chemical attraction. The action of ammonic sulphate on calcic carbonate affords a case in point. If these two salts be mixed in a dry state, at ordinary temperatures, they do not appear to act upon each other; but if gently heated, decomposition ensues, and ammonic carbonate and calcic sulphate are produced; the ammonic carbonate is expelled, and being volatile is removed from the mixture; $CaCO_3 + (NH_4)_2SO_4$ yielding $(NH_4)_2CO_3 + CaSO_4$. But suppose a solution of calcic sulphate to be mixed with one of ammonic carbonate, the effects are exactly reversed; calcic carbonate is precipitated, whilst the soluble ammonic sulphate remains in the liquid; and now $(NH_4)_2CO_3 + CaSO_4$ become $CaCO_3 + (NH_4)_2SO_4$.

A remarkable illustration of the important influence exerted by volatility in counteracting powerful chemical attractions, is afforded in the decomposition of the sulphates by weaker acids at a high temperature:—for example, the action of sulphuric acid upon bases is of the most energetic kind, whilst that of boric acid, on the contrary, is extremely feeble. If a solution of borax be mixed with sulphuric acid, the sodium of the salt will change places with the hydrogen of the sulphuric acid as it is added, whilst boric acid will gradually be separated, and if the liquid be hot and not too concentrated, will be retained in solution. Owing to the peculiar action of boric acid on blue

litmus, it can be shown that the two acids do not divide the sodium between them, for if a piece of blue litmus-paper be placed in the liquid, it will exhibit the peculiar wine-red tint due to boric acid, until a quantity of sulphuric acid exactly equivalent to the sodium contained in the borax has been added; but the moment that this point is reached, an excess of sulphuric acid immediately reveals itself by the change of the colour of the litmus from dusky purplish-red to a bright red. It is therefore clear that boric acid cannot effect even a partial displacement of sulphion from its combination with sodium when the two are in solution. But it is otherwise at a red heat: if boric anhydride be fused with sodic sulphate, borax is produced, and sulphuric anhydride, which is volatile at this high temperature, is expelled in the gaseous form. Other acids and anhydrides which are known to have a feebler attraction for bases than sulphuric acid, but which support a red heat without being volatilized, such as phosphoric and silicic anhydrides, are also able to decompose the sulphates when heated with them.

In like manner, when a base which is fixed is heated with the salt of a volatile base, the volatile base is displaced by the more fixed one; thus, quicklime or potassic hydrate, if heated with an ammonium salt, is converted into a calcic or potassic salt, whilst water and gaseous ammonia are expelled; $2NH_4Cl + CaO = CaCl_2 + OH_2 + 2NH_3$.

(1218) **Effect of Mechanical Action on Chemical Attraction.**—The effect of volatility in removing from the sphere of action one of the components of a body which is undergoing decomposition, may in some cases be considerably assisted by mechanical means; and when the attractions of the displacing body, and of the substance displaced by it, for the other constituent of the compound, are nearly equal, effects which are in apparent opposition to each other, may sometimes be produced. For instance, ferric oxide, when heated to redness in a current of hydrogen gas, is gradually reduced to the metallic state: the steps of the process appear to be these:—A small quantity of water is formed; it immediately diffuses itself in vapour into the hydrogen, and is mechanically carried away by the current of the gas, and this process goes on until the reduction is complete. On the other hand, if metallic iron be heated in a current of steam, water is decomposed, hydrogen is liberated, and is carried beyond the reach of chemical action upon the newly formed oxide of iron by the excess of the steam employed. In a similar manner, if a current of sulphuretted hydrogen in large excess be

passed over solid hydric potassic carbonate, gently heated, carbonic anhydride and water will be displaced from the acid-carbonate, and carried forward by the excess of the gas, whilst dipotassic sulphide will be formed: $2KHCO_3 + SH_2 = 2CO_2 + 2OH_2 + K_2S$. But if a current of carbonic anhydride be passed through an aqueous solution of dipotassic sulphide, this in its turn will be gradually but completely decomposed, the sulphuretted hydrogen being carried away by the excess of carbonic anhydride, whilst hydric potassic carbonate is formed in the liquid: $K_2S + 2CO_2 + 2OH_2 = SH_2 + 2KHCO_3$.

(1219) **Influence of Pressure.**—The influence of pressure upon the formation of compounds is well exemplified in the following instances:—Wöhler (*Ann. Chem. Pharm.*, 1853, lxxxv. 376) found that a hydrate of sulphuretted hydrogen may be obtained in colourless crystals, if a portion of persulphide of hydrogen, free from acid, be sealed up in a strong glass tube with a small quantity of water; the persulphide gradually undergoes decomposition into crystallized sulphur and gaseous sulphuretted hydrogen, the gas combines with the water, and forms a crystalline solid, which disappears with effervescence when the tube is heated to 30° (86° F.), but is reproduced on cooling. If a tube containing crystals of this compound be opened, the crystals immediately disappear with brisk effervescence. Hydrate of chlorine, under ordinary circumstances, becomes liquid at a few degrees above the freezing-point of water, with escape of gaseous chlorine; but if the solid hydrate be sealed up in a glass tube, it remains solid even when the temperature rises as high as 20° (68° F.), the pressure of the chlorine within the tube retarding the decomposition. Again, calcic carbonate is decomposed in an open fire, at a red heat, into carbonic anhydride and quicklime; but if it be inclosed in an iron tube, the mouth of which is plugged to prevent the escape of the gas, the carbonate may be melted, and on cooling it furnishes a granular mass, which is still calcic carbonate, and has the appearance of marble (Sir J. Hall).

(1220) **State of Salts in Solution.**—The application of thermic methods has enabled us to some extent to ascertain what takes place when a salt is dissolved, for this is almost invariably accompanied by a sensible development or absorption of heat, due to a variety of causes; for instance, in the case of a hydrated crystalline compound, like sodic sulphate, $Na_2SO_4.10OH_2$, it may be conceived that there is a disaggregation of the molecules which compose the crystal, and, moreover, that there is an effect comparable to fusion. The latter is of a complex nature and

may be accompanied by a dissociation of the molecules themselves, or by the separation of the water of crystallization, or by the addition of more water. The investigation of these phenomena is, however, a problem of considerable difficulty, since the thermal changes merely represent the final result, and this may be due to the difference between the heat developed by one action such as that of hydration, and that absorbed by another such as dissociation.

When a salt is dissolved in water, there is usually a contraction, the total volume being less than that previously occupied by the water and the salt together; this is the joint effect of the contraction of the solvent under the influence of the salt, and the increase in volume of the salt caused by dissociation; for in only very few instances, such as those of ammonic chloride, bromide, and iodide, does the latter effect exceed the contraction produced in the solvent, thereby rendering the total volume greater. The total contraction is generally less than the volume of the body dissolved, so that when an equivalent in grams of any compound is dissolved in a litre of water, the volume of the solution is greater than a litre. There are, however, some exceptions; aluminic sulphate and sodic carbonate do not sensibly increase the volume of the liquid, whilst in the case of potassic and sodic hydrates there is an absolute contraction; the solution of 1 equivalent (in grams) of potassic hydrate in 1 litre of water measuring only ·996 litre, and that of sodic hydrate ·987 litre. It would seem also from the experiments of Favre and Valson (*Compt. Rend.*, 1873, lxxvii. 577), that when a salt is dissolved, each of its saline radicles produces an increase of density proper to itself, and quite independent of the other radicle with which it may be associated.

When an acid salt of a monobasic acid, such as potassic binacetate, is dissolved in water it is completely decomposed into the neutral salt and free acid; acid salts of polybasic acids, however, are only partially split up, the quantity of salt decomposed increasing slowly and continuously with the dilution; moreover, when an excess of either the neutral salt or free acid is present in the solution, it tends, as may readily be conceived, to retard the decompositon of the acid salt. Salts formed by the union of weak acids and weak bases, are more or less decomposed when dissolved in water, the solution containing free acid, free base, and undecomposed salt. In the case of the ferric salts, the decomposition is almost complete, and on submitting such a solution to dialysis the acid can be removed and a peculiar modification

of ferric oxide left in solution (p. 646). Elevation of temperature has also a marked effect on the decomposition of salts in solution, and this is especially observable with the ferric salts. It seems, however, that salts formed by the union of strong acids and strong bases, as the sulphates, chlorides, and nitrates of potassium, undergo no change when dissolved.

When double salts are dissolved in water the cold produced by their solution is greater than the sum of that produced by the two salts dissolved separately. This is easily accounted for by the fact that a certain amount of energy is involved in the formation of the double salt, and this is represented by the heat absorbed by its dissociation when dissolved. It is evident therefore that double salts are generally resolved into their constituent salts when dissolved in water: this is especially the case with the alums.

(1221) **Action of Acids on Salts in Solution.**—Whenever an acid—that is to say, a salt of hydrogen—is added to the solution of a salt with the basyl of which the oxion or radicle of the added acid is capable of forming a soluble compound, it generally produces a partial exchange of its basic hydrogen with the basyl of the salt originally in solution, so that two acids and two salts may be present in the liquid, in some unknown proportions depending upon the strength of the relative attractions of the metal for the radicles of the two acids: when, for example, potassic nitrate is mixed with sulphuric acid, part of the potassium exchanges places with the hydrogen of the sulphuric acid, and part remains united with the nitrion, whilst a portion of nitric acid will be liberated, and will become mixed with the uncombined sulphuric acid: for example, $3H_2SO_4 + 5KNO_3 = H_2SO_4 + KHSO_4 + K_2SO_4 + 3HNO_3 + 2KNO_3$. The occurrence of such a decomposition as this, however, in many cases does not admit of direct proof. If an additional force be called into operation, as is the case on the application of heat, the more volatile acid may be expelled in the form of vapour, and may thus be withdrawn from the sphere of action. In cases where the attraction of the radicle of one acid for the metallic basyl is very strong, whilst that of the other is feeble, the radicle of the stronger acid may (as in the case of sulphuric acid and borax, already cited, or in that of nitric or hydrochloric acid and sodic acetate) be supposed to appropriate the basyl entirely to itself. This, however, is not always so, as has been shown by Hübner (*Pog. Ann.*, 1867, cxxxi. 55; and *Jubelband*, 182). A weak acid may partly displace a stronger one, and if the aqueous solution be agitated with a liquid such as chloroform or benzene, in which either the weaker

or the stronger acid is more readily soluble than in water, then a portion of the acid will be removed, and the displacement will progress or regress, according as the stronger or the weaker acid is removed. Sometimes the occurrence of such a partition can be proved by the change of colour which ensues after the mixture has been effected. Cupric sulphate, for example, is of a blue colour when in solution, and cupric chloride is green. If a solution of the blue sulphate be mixed with hydrochloric acid, it is evident that the copper enters partially into combination with the chlorine of the hydrochloric acid, since the solution assumes a bright green tint; $2CuSO_4 + 4HCl = CuSO_4 + CuCl_2 + H_2SO_4 + 2HCl$.

If the basyl form an insoluble compound with the radicle of the newly added acid, it is possible to decompose the original salt completely by its means. If, for instance, a solution of baric nitrate or acetate be mixed with sulphuric acid, it may be supposed that the barium divides itself between the two oxions in proportion to its attraction for each; but since baric sulphate is insoluble, it is at once withdrawn from the mixture, and the barium remaining in the original salt again divides itself between the two oxions; the fresh portion of baric sulphate, however, is immediately precipitated; and so, by a series of steps which, where the chemical attractions are strong, succeed each other very rapidly, the whole of the barium is separated in the form of an insoluble sulphate, leaving the nitric or the acetic acid free in the solution.

A very feeble acid may even displace a more powerful one when the compound which it forms is insoluble in the menstruum in which it is suspended. Hydrocyanic acid will separate nitric acid from argentic nitrate, owing to the formation of the insoluble argentic cyanide; $AgNO_3 + HCy = HNO_3 + AgCy$. Tartaric acid will liberate sulphuric acid in a solution of argentic sulphate, owing to the formation of an insoluble argentic tartrate. Oxalic acid will precipitate cupric oxalate from a solution of cupric chloride; and Pelouze has observed that, if a current of carbonic anhydride be passed through a solution of potassic acetate dissolved in alcohol, acetic acid will be liberated, and potassic carbonate, which is insoluble in alcohol, will be separated; but no such change occurs in its aqueous solution, since potassic carbonate is freely soluble in water. This rule, however, is not without exception, where one acid is very powerful and the other is very feeble; calcic borate, for instance, is an insoluble salt, but a solution of boric acid will not occasion any precipitate if mixed

with one of calcic nitrate; calcic citrate and tartrate are also insoluble compounds, but neither solution of citric nor of tartaric acid occasions a precipitate in one of calcic nitrate.

In like manner, if the acid originally present be insoluble in water, it will be separated, and the salt will be decomposed; for example, on the addition of nitric acid to a solution of potassic tungstate, the tungstic acid is precipitated, whilst potassic nitrate is retained in the solution; $2HNO_3 + K_2WO_4 = 2KNO_3 + H_2WO_4$.

(1222) **Action of Bases on Salts in Solution.**—An analogous decomposition occurs if a quantity of some additional base be added to a saline solution. If the two bases be soluble, and the salts which they form be also soluble, the solution will remain clear, and it may be supposed that the acid radicle is divided between the metals of the two bases in proportion to its attraction for each, as when a solution of baric nitrate is mixed with a solution of potassic hydrate: a mixture of baric and potassic nitrates with baric and potassic hydrates is thus obtained; but as baric hydrate is less soluble than potassic hydrate, a portion of baric hydrate will be gradually deposited if the solutions be in a concentrated form. If either of the bases be insoluble, or form an insoluble salt with the acid, a complete separation of the base or of the acid contained in the original salt may almost always be effected.* For example, the salts of nearly all the metals, with the exception of those of the alkalies and of the alkaline earths, are derived from metallic oxides which are not soluble in water: the addition of any soluble base, such as potassic, or sodic hydrate, or ammonia to their solutions, immediately occasions the precipitation of the insoluble oxide, or of its corresponding hydrate. It is in this manner that such oxides are commonly prepared; for example, oxide of zinc, iron, cobalt, nickel, manganese, or silver, may thus be completely separated from the acid by which it was previously held in solution; for instance, $2KHO + CoSO_4 = CoH_2O_2 + K_2SO_4$. Solutions of the hydrates of baryta, strontia, or lime, act in a similar manner, if the acid be one which, like nitric or hydrochloric, is capable of furnishing a soluble compound by its action upon these bases. A solution of cupric nitrate may thus be decomposed by a solution of baric hydrate; $Cu2NO_3 + BaH_2O_2 = Ba2NO_3 + CuH_2O_2$.

* Berthelot has found, however (*Compt. Rend.*, 1875, lxxx. 1564), that ammonic chloride offers a remarkable exception to this law, for when treated in aqueous solution with calcic hydrate the ammonia is entirely displaced and calcic chloride formed: here the sparingly soluble calcic hydrate has entirely displaced the easily soluble ammonia.

In a few cases, no precipitation occurs even where the oxide is insoluble; when, for instance, mercuric cyanide is mixed with a solution of potassic hydrate, no precipitate is produced, although mercuric oxide is insoluble in water.

If the newly added base form an insoluble compound with the acid, it is wholly precipitated by it; and if the other base be soluble, it remains in the liquid. One of the methods of obtaining a solution of pure potassic hydrate is founded on this principle; in this experiment, a solution of potassic sulphate is mixed with a quantity of a solution of baric hydrate exactly sufficient to precipitate the whole of the sulphuric acid; $BaH_2O_2 + K_2SO_4 = 2KHO + BaSO_4$; and in a similar manner potassic oxalate is deprived of its oxalic acid by the addition of lime-water to its solution, owing to the formation of an insoluble calcic oxalate. If the base as well as the salt which is formed by the addition of the new base to the acid be insoluble, it is possible to precipitate the whole of both acid and base from the liquid simultaneously; as when a solution of baric hydrate is added in the proper proportion to a solution of argentic sulphate; $BaH_2O_2 + Ag_2SO_4 = 2AgHO + BaSO_4$.

(1223) **Mutual Action of Salts in Solution.**—It is a rule almost without exception,* *that when solutions of two salts, capable of forming, by interchange of their acid radicles and basyls, an insoluble or sparingly soluble salt, are mixed, the salts decompose each other, and the compound which is least soluble is precipitated.* It is in this manner that the greater number of insoluble compounds are formed by the process of double decomposition. Argentic iodide, for instance, is thus obtained by acting upon a solution of argentic nitrate with one of potassic iodide; $AgNO_3 + KI = KNO_3 + AgI$; and in a similar manner, if manganous carbonate or tricupric diphosphate be required, it may be prepared by mixing a solution of manganous chloride or of cupric sulphate with one of potassic carbonate or of hydric disodic phosphate. Sometimes a soluble compound may be advantageously obtained in this manner, as in the ordinary method of preparing aluminic acetate, in which a solution of plumbic acetate is mixed with one of aluminic sulphate: plumbic sulphate is precipitated, and aluminic acetate remains in solution; $3Pb2C_2H_3O_2 + Al_23SO_4 = 3PbSO_4 + Al_26C_2H_3O_2$.

* When a solution of mercuric cyanide is mixed with one of argentic nitrate, little or no precipitate is produced, although argentic cyanide is a very insoluble compound, and mercuric cyanide has not the power of forming a soluble double cyanide with it.

When two saline solutions are mixed, which, by the interchange of their acid radicles and basyls, form compounds also freely soluble, it has been found by Berthelot (*Compt. Rend.*, 1866, lxiii. 1056; and 1873, lxxvi. 94) that the strong acids usually combine with the strong bases, and the weak acids therefore with the weak bases, so that the salt which is most stable in presence of water is formed, and also the one which is least stable. In most cases, however, it is impossible to state with certainty what are the salts which are present in any solution which contains a number of saline compounds. In the analysis of a mineral water, for example, it is possible to determine the amount of each acid radicle and of each basyl which is present, but it is not possible to say what the salts really were which were brought into solution to form the mineral water in question. Sulphion, nitrion, carbon, and chlorine may have been present amongst the acid radicles, and potassium, sodium, calcium, and magnesium amongst the basyls; but it is impossible to say how all these radicles and basyls are distributed in the solution. Many chemists allot the basyls to the acid radicles in the order of the insolubility of the different salts, whilst others allot the strongest basyls to the strongest radicles. In reporting the results of analysis, however, the quantities of the separate salt radicles and basyls should invariably be given: in addition to which, the analyst, if he pleases, can allot them according to his fancy. The foregoing remarks may be illustrated by the curious alternate decompositions which differences of solubility at different temperatures sometimes bring about: a striking instance of this kind occurs in the case of a mixture containing both magnesic sulphate and common salt. These salts occur mixed together in the mother-liquor of sea-water, after the bay-salt has been separated on the large scale. Four salts may be formed by the intermixture of these two compounds, viz., magnesic sulphate, sodic sulphate, magnesic chloride, and sodic chloride. Of these four salts, sodic chloride is the least soluble at the boiling-point; if, therefore, the solution be concentrated by ebullition, sodic chloride is separated in crystals; and as the liquid cools, the magnesic sulphate crystallizes out. The effect, however, will be different if the solution be allowed to evaporate spontaneously in the open air; at low temperatures the sodic sulphate is the least soluble of the four salts; and at low temperatures it is the sodic sulphate which separates in crystals from the liquid, whilst the readily soluble magnesic chloride remains in solution (p. 436).

Upon a similar principle sodic nitrate is converted on a large

scale into potassic nitrate, by acting on it with potassic chloride (p. 419); on concentrating the solution by boiling, sodic chloride is separated in crystals, and potassic nitrate crystallizes out as the liquid cools: at low temperatures sodic chloride is more soluble than potassic nitrate, and the nitre crystallizes out nearly in a state of purity.

It may, in fact, be stated as a general principle, that on concentrating a mixed solution by evaporation, the salt which is least soluble at the particular temperature employed is that which will be formed.

In certain cases where there is no great difference in the solubility of two salts, evidence is yet afforded of the mutual decomposition when the solutions are mixed, by the change of colour which then takes place. Potassic sulphocyanide, for example, when mixed with a solution of ferric chloride, so much diluted as to be colourless, indicates by the blood-red solution which it forms, that a partial interchange of the components of the two salts has been effected. In a manner somewhat similar, when a solution of ferrous sulphate is mixed with one of sodic acetate, sulphuretted hydrogen causes the precipitation of the iron as ferrous sulphide. This reaction could only take place owing to the formation of ferrous acetate, since a solution of ferrous acetate admits of being thus decomposed by sulphuretted hydrogen, but one of ferrous sulphate is not so acted upon. The whole of the iron may be separated in this manner, for no sooner is a certain proportion of the iron rendered insoluble, than a fresh portion of ferrous acetate is formed: and this formation and decomposition of the salt continues as long as any iron remains in solution.

(1224) **Influence of Mass in the Formation of Chemical Compounds.**—A curious question presents itself as to the proportion in which two bodies are capable of thus decomposing each other on mixture. When, for example, three different bodies, A, B, and C, are mixed together, one of which, C, is capable of combining with either of the other two, and forming with them compounds, A C, B C, which in both cases are soluble, the quantity of A and of B being considerably in excess of C,—will the proportion in which C enters into combination with A and B, be determined merely by the strength of their relative chemical attraction? or will the proportion in which each of these bodies is present also influence the result? It was argued by Berthollet, that not only would C be divided between A and B, but that in proportion as the quantity of one of these bodies, A, preponderated over the

other body, B, the proportion of A C in the mixture would be increased, while, of course, that of B C would be diminished. If, on the other hand, the proportion of B were increased, the quantity of the compound B C would be augmented, whilst that of A C would be proportionately lessened, the body C dividing itself between A and B, in a proportion represented by the product of its chemical attraction for each of these elements multiplied into their mass. Thus if a represent the mass of A, let x represent its chemical attraction for C; if β be the mass of B, and y its chemical attraction for C; then $ax : \beta y :: A C : B C$. Suppose, for example, a solution of potassic nitrate to be mixed with more than its equivalent of sulphuric acid; it is generally conceded that the potassium divides itself between the two acids, forming a mixture of potassic sulphate and nitrate, with free sulphuric and nitric acids. Now if the quantity of sulphuric acid be increased, will the quantity of potassic sulphate which is thus formed be influenced by the amount of sulphuric acid which is thus added in excess? and if so, to what extent will this influence of the *mass* of the acid modify the simple effect of chemical attraction.

Let us imagine, for example, that x, the attraction of sulphion for potassium, $=5$, whilst y, that of nitrion for potassium, $=4$. When an equivalent of sulphuric acid is presented to an equivalent of potassic nitrate, the mass a of sulphuric acid $=1$: that of the nitric acid $\beta=1$ also. Then $ax : \beta y$ as $5 : 4$. The nitrate will be partially decomposed; $\frac{5}{9}$ of the potassium will enter into combination with the sulphion, whilst $\frac{4}{9}$ will be united with nitrion, and we shall have in the solution $\frac{5}{9}$ (K_2SO_4), $\frac{4}{9}$ ($2KNO_3$), $\frac{4}{9}$ (H_2SO_4) and $\frac{5}{9}$ ($2HNO_3$). But suppose, instead of adding 1 equivalent of sulphuric acid, 2 equivalents be employed, whilst the proportion of the nitrate remains unaltered; the mass a of the sulphuric acid is now 2, and $ax : \beta y$ as $10 : 4$. The proportion of potassic nitrate will be diminished, and there will be $\frac{10}{14}$ (K_2SO_4), $\frac{4}{14}$ ($2KNO_3$), $1\frac{4}{14}$ (H_2SO_4), and $\frac{10}{14}$ ($2HNO_3$); and if 3 equivalents of sulphuric acid be employed to 1 of potassic nitrate, since the mass a of sulphuric acid is now $=3$; $ax : \beta y$ as $15 : 4$; consequently the proportions of the ingredients would be $\frac{5}{19}$ (K_2SO_4), $\frac{4}{19}$ ($2KNO_3$), $2\frac{4}{19}$ (H_2SO_4) and $\frac{10}{19}$ ($2HNO_3$): the proportion of potassic sulphate continuing to increase, although in a decreasing ratio, for every addition of free sulphuric acid to the solution.

(1225) **Gladstone's Experiments on Mass.**—No experimental solution of this problem was given by Berthollet, and the question fell into abeyance; but within the last few years several

attempts have been made with considerable success to determine this question quantitatively. Gladstone (*Phil. Trans.*, 1855, p. 179) has published a series of experiments in which he has made use of the change of colour which solutions of certain salts undergo on mixture with each other, as a means of ascertaining the extent to which this mutual decomposition proceeds when all the products remain in solution. The principle of his experiments will be easily understood. Solutions of several ferric salts, such as the ferric sulphate, nitrate, chloride, acetate, citrate, &c., were prepared in such a manner that each should contain the same proportion of iron dissolved in the same bulk of water (each of the solutions employed contained a quantity of iron corresponding very nearly to 1 part of ferric oxide in 1000 parts of water). A solution of pure potassic sulphocyanide was then prepared of such a strength that when 1 measure of this solution and 4 of that of the ferric salts were mingled, the proportion of sulphocyanogen should be exactly sufficient to convert the whole of the iron into sulphocyanide, if complete mutual decomposition occurred: thus the proportions of the two salts employed were such that it would be possible for exact mutual interchange to occur as represented in the following equation: $Fe_2 6NO_3 + 6KScy = Fe_2Scy_6 + 6KNO_3$. On making the experiment in this manner, it was found that the iron was never wholly converted into the red salt, for the tint was deepened by the addition of more either of the ferric salt or of the sulphocyanide. In order to obtain a quantitative estimate of the amount of these effects, definite measures of the solutions of ferric nitrate and of potassic sulphocyanide were mixed together, and the liquid so obtained was diluted with water until it occupied a known, but arbitrary volume. This diluted mixture furnished a liquid of a certain depth of colour which was employed as a standard of comparison. Another measure of the solution of ferric nitrate, equal to that used in the standard solution, was mixed with regulated additions of the potassic sulphocyanide, and the liquid thus obtained was diluted with measured quantities of water after each addition of sulphocyanide, until, as far as the eye could distinguish, this solution had the same depth of tint as that employed as the standard; it was then assumed that the quantity of ferric sulphocyanide formed was proportionate to the bulk of the two solutions.* Suppose that the

* Gladstone found that simple dilution of the ferric sulphocyanide reduced the tint in a proportion greater than could be accounted for by mere dilution; but this source of error was eliminated, and was not found to present itself in other cases which he employed to test the accuracy of the general conclusion.

standard solution occupied a volume of 880 measures: it was found that if twice the quantity of the potassic sulphocyanide employed in the standard liquid were made use of in the new solution, this mixture would require dilution until it occupied 1270 measures. The proportion of ferric sulphocyanide formed in these two cases was assumed to be as 880 to 1270, or as 1 to 1·44. The excess of sulphocyanide thus employed had therefore withdrawn an additional quantity of iron from its combination with the nitric acid.

In this manner experiments were made with quantities of the potassic sulphocyanide, progressively increasing from one-fifth of an equivalent of the sulphocyanide to each equivalent of ferric nitrate, up to 375 equivalents of sulphocyanide to 1 equivalent of ferric nitrate, and it was found that the quantity of ferric sulphocyanide which was formed, continued to increase with every addition of potassic sulphocyanide, although the effect of each consecutive addition became less and less marked.

It was ascertained, as indeed it was to be expected, that the proportions of ferric sulphocyanide, which are formed by the mixture of equivalent quantities of other salts of iron with given amounts of the potassic sulphocyanide, vary with the nature of the acid radicle contained in the ferric salt. For example, it was found that when ferric nitrate was mixed with potassic sulphocyanide, in the proportion of equivalent quantities of each, that 0·194 of an equivalent of the red salt was formed. When an equivalent of ferric chloride was used, 0·173 of an equivalent was formed; when ferric sulphate was employed, 0·126 of an equivalent was produced; with ferric acetate 0·04 only was formed; and when ferric citrate was employed, the quantity of ferric sulphocyanide which it yielded was too small to admit of being estimated. The iron therefore retained the radicles of these different acids with degrees of force which vary inversely with the quantity of ferric sulphocyanide which is formed, whilst the potassium in the sulphocyanide attracted them with a power in direct proportion to these quantities. Various attempts have been made to obtain relative numerical expressions for the force of chemical attraction by which different compounds are united, but they have all hitherto failed.

Besides the ferric sulphocyanide, Gladstone examined a variety of other coloured compounds; one of these was the scarlet auric bromide, which becomes yellow when mixed with potassic and sodic chlorides, to an extent varying with the proportion in which these salts are added: quinine sulphate, when mixed with a

soluble chloride, bromide, or iodide, also afforded similar indications, as it loses its fluorescent character (110) in proportion to the quantity of chloride or bromide with which it is mixed. From these and from a variety of other experiments, it appears that when two or more compounds in solution are made to act upon each other, provided that the products which they form by their mutual action are also soluble, the following conclusions may be drawn:—1. That mutual interchange between the bodies which are mixed takes place in determinate proportions. 2. That these proportions are independent of the manner in which the compounds were originally combined: thus, if potassic sulphate and ferric nitrate be mixed in equivalent quantities, the result is the same as if potassic nitrate and ferric sulphate had been employed in equivalent quantities. 3. That these proportions are dependent partly upon the strength of the mutual attractions of the components for each other, and partly also upon the *mass*, or relative proportion of each compound which is present in the mixture. 4. That the alteration of the mass of any one of these compounds alters the amount of all the other compounds which co-exist in the mixture, in a regularly progressive ratio; and these quantities admit of being represented by regular curves. In most cases this adjustment of the relative quantities of the different bodies takes place immediately that the mixture is made.

(1226) **Experiments of Bunsen and of Debus.**—The results are different if the products of the chemical combination be at once removed from the sphere of action,—as by the formation of gaseous compounds, or of an insoluble precipitate when two liquids are mixed. Bunsen has investigated the results obtained in some cases of gaseous combination. He found that when a mixture of hydrogen and carbonic oxide was detonated with oxygen in quantity insufficient for its complete combustion, the oxygen divided itself between the two gases in such a manner that the quantities of water and of carbonic anhydride produced were in very simple atomic relations to each other (*Ann. Chem. Pharm.*, 1853, lxxxv. 137). He exploded mixtures of oxygen, hydrogen, and carbonic oxide, in varying proportions, the hydrogen and carbonic oxide being each in considerable excess over the oxygen: under such circumstances water and carbonic anhydride were formed: but the quantity of carbonic anhydride was greater, in proportion as the carbonic oxide preponderated, according to a certain law. Similar results were obtained by detonating cyanogen with a quantity of oxygen insufficient for its complete combustion; in this case nitrogen and a mixture of carbonic anhydride

and carbonic oxide in simple proportions were obtained: and when a mixture of carbonic anhydride and hydrogen was detonated with a quantity of oxygen insufficient for the consumption of the hydrogen, a certain proportion of the carbonic anhydride was reduced to carbonic oxide, according to the terms of the same law.

The following is the law deduced by Bunsen from his experiments:—1. When two gaseous bodies, A, B, are mixed with a third body, C, and fired by means of the electric spark, the body C takes from A and B quantities which always stand to one another in a simple molecular relation: so that for 1 molecule of A C, 1, 2, 3 or 4 molecules of B C are produced; for 2 molecules of A C, 3, or 5, or 7 molecules of B C are formed. If 1 molecule of the compound A C, and one of B C be formed in this manner, the mass of A may be increased in the presence of B, up to a certain point, without any change in that molecular proportion; but if a certain limit be passed, the relation of molecules, instead of being as 1 : 1, suddenly becomes as 1 : 2, or as 2 : 3; and so on.

2. When a body, A, acting upon an excess of any compound, B C, reduces it, so that A C is formed, and B is set at liberty; then—if B in its turn can reduce the newly formed compound, A C—the final result is, that the reduced part of A C is in simple molecular proportion to the unreduced part. In the case of these reductions also, the mass of one of the ingredients of the mixture may be increased up to a certain point without altering the relative proportions of the compounds obtained; but if increased beyond this limit, a sudden alteration in the relative proportions of the products occurs; but these proportions still admit of being represented by simple ratios. This second portion of the law needs confirmation by more extended experiments.

The following experiments illustrate the first part of the foregoing law:—On exploding mixtures of carbonic oxide and hydrogen with oxygen, in the following proportions, Bunsen found that the quantities of carbonic oxide and hydrogen which were oxidized were in the proportions stated below:

	Mixture detonated.			Ratio of gases burned.	
	Oxygen.	Hydrogen.	Carb. oxide.	Hydrogen.	Carb. oxide.
I. ...	10 ...	20 ...	79·4 ...	1 :	2
II. ...	10 ...	20 ...	44·4 ...	2 :	2
III. ...	10 ...	20 ...	12·1 ...	6 :	2
IV. ...	10 ...	37 ...	31·5 ...	8 :	2

These experiments show that, as the proportion of carbonic

oxide to the hydrogen in the mixture decreased, the proportion oxidized on detonation decreased also, but it decreased *per saltum*, not gradually, and these proportions were found to be uniformly the same on repeating the detonation with the same mixture, although the degree of compression to which the mixture was subjected during the detonation was considerably varied in different experiments.

The following are Bunsen's principal experiments in support of the second part of the foregoing law:—When carbonic anhydride is passed over ignited charcoal, it is wholly converted into carbonic oxide; but when steam is passed over ignited charcoal, a mixture of hydrogen, carbonic oxide, and carbonic anhydride is produced, in the proportion of 4 volumes of hydrogen, 2 of carbonic oxide, and 1 volume of carbonic anhydride. Again, when a mixture of cyanogen with atmospheric air and oxygen was detonated in the eudiometer in the proportion of 6·2 of cyanogen to 10 of oxygen,* the cyanogen yielded 3 volumes of nitrogen, 2 of carbonic oxide, and 4 of carbonic anhydride: and when a mixture of 4·07 of carbonic anhydride, 33·25 of hydrogen, and 10 of oxygen was detonated, a portion of the carbonic anhydride yielded oxygen to the hydrogen, and was reduced to the state of carbonic oxide; 3 volumes of carbonic oxide being formed, whilst exactly 2 volumes of carbonic anhydride remained unacted upon, although a large excess of hydrogen was present.

E. Meyer (*Jour. pr. Chem.*, 1874, ccx. 273) has since made an extended series of experiments in the same direction, which entirely confirm the results obtained by Bunsen, and that, whether nitrous oxide be substituted for oxygen, or whether the mixture be diluted with an indifferent gas such as nitrogen. When a mixture of carbonic oxide and hydrogen in fixed proportions is burned in a wide eudiometer with varying quantities of oxygen, the co-efficient of affinity reaches a maximum when the smallest possible quantity of oxygen is used, which will render the mixture explosive. When the mixture is diluted with an indifferent gas, the affinity of the hydrogen to oxygen is diminished, whilst that of carbonic oxide to oxygen increases in a corresponding degree.

Debus arrived at substantially the same results with preci-

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* Cyanogen requires for the complete combustion of its carbon twice its volume of oxygen, so that 6·2 of cyanogen would have required 12·4 instead of 10 of oxygen: there is therefore more oxygen than would suffice for the conversion of the carbon into carbonic oxide.

pitates as those indicated by Bunsen for gaseous mixtures:—he precipitated a mixture of lime and baryta water, by small proportions of a solution of carbonic acid; and experiments upon a large excess of a dilute solution of the mixed calcic and baric chlorides to which a dilute solution of sodic carbonate was added, led to a similar result.

In the experiments of Bunsen, it must be recollected that the first products of the chemical combination are immediately removed from the sphere of action: carbonic anhydride, and carbonic oxide, and water will not mutually react upon each other; and in the experiments of Debus, the carbonates of the metals of the earths are insoluble—they are therefore at once withdrawn from further action upon the mixture.

(1227) **Harcourt and Esson's Experiments.**—Messrs. Harcourt and Esson have attacked this problem in a different way (*Phil. Trans.*, 1866, 193; 1867, 117):

Every chemical reaction is governed by certain general laws relating to the *quantity* of the substances which enter into it, their *temperature*, their *physical state*, and the *time* during which they are in contact: yet the number of cases admitting of exact investigation is very limited. It must be possible to begin and end the reaction abruptly at a given moment so as to limit the time exactly; and it must be possible to determine accurately and easily one at least of the products of the reaction, so that the amount of the chemical change can be measured.

These conditions they attempted to fulfil by investigating the reaction of oxalic upon permanganic acid. This action, however, was found not to be sufficiently simple; and after a laborious series of experiments they ascertained that another reaction, viz., that of hydric peroxide upon hydriodic acid, was better adapted to the purpose.

When solutions of potassic iodide and sodic peroxide are mixed in the presence of sulphuric acid a *gradual* separation of iodine takes place, sodic and potassic sulphates are formed, and the liberated hydric peroxide and hydriodic acid undergo a change which may be thus represented: $H_2O_2 + 2HI = 2H_2O + I_2$. If sodic thiosulphate be added to the solution it *instantly* reconverts the iodine into hydriodic acid, but although the thiosulphate passes into a tetrathionate it appears in no way to affect the course of the reaction:

$$\overbrace{2H_2S_2O_3}^{\text{Thiosulphuric acid.}} + I_2 = \overbrace{H_2S_4O_6}^{\text{Tetrathionic acid.}} + 2HI.$$

Consequently, if the peroxide be in excess over the thiosulphate, the whole of the thiosulphate is gradually changed by the nascent iodine into tetrathionate; whilst the amount of hydriodic acid remains constant, and after the conversion of the thiosulphate is complete, free iodine again makes its appearance in the solution by the gradual action of the excess of hydric peroxide upon the hydriodic acid. The moment at which this liberation of iodine occurs can be most accurately observed by the previous addition of a little starch to the mixture.

In performing the experiment, measured quantities of the standard solutions of sulphuric acid, potassic iodide, and a filtered solution of starch were diluted with pure distilled water, previously boiled to free it from air, and allowed to cool in a vessel filled with carbonic anhydride, the glass cylinder in which the mixture was made being always filled up with the liquid to a given mark upon its side. A definite small measure of a solution of sodic thiosulphate was then added, and the reaction was commenced by the addition of 10 cub. centim. of a standard solution of sodic peroxide acidulated with sulphuric acid. The mass was kept continually agitated by the transmission of a stream of bubbles of carbonic anhydride, and the temperature was maintained uniform during the period of experiment. As soon as the blue colour manifested itself, a note of the time was made, and a second measure of thiosulphate was added, by which the colour was instantly bleached, and the interval of time noted before the blue colour reappeared. A third measure of thiosulphate was then added, and so on in succession. The time that elapses between two successive appearances of the blue colour becomes continually greater in proportion as the amount of peroxide in the solution diminishes; finally, the last measure of thiosulphate requires for conversion into tetrathionate more oxygen than the peroxide can furnish, and the blue colour never returns.

By these experiments it was found that the amount of action varies directly with the variation in the amount of the active substance, the rate of action becoming slower as the quantity of peroxide diminishes. Harcourt and Esson state their general conclusion as follows:—'The amount of change varies directly (1) with the amount of iodide, and (2) with the amount of peroxide in a unit volume of the solution; (3) with the time during which the change proceeds; (4) with the total volume of the solution; and finally, with some function of each of the other conditions under which the change occurs.'

(1228) **Surface Action of Platinum.**—The adhesion of gases to solids produces many curious phenomena:—for example, let a piece of charcoal be thoroughly saturated with hydrogen by attaching it to the negative wire of the voltaic battery, and employing it as the platinode in the decomposition of acidulated water; this charcoal, if now detached from the battery and thrown into a solution of cupric sulphate, or of argentic nitrate, will effect the decomposition of these salts, and copper or silver will be thrown down upon the charcoal in the reduced state; the charcoal and condensed hydrogen appearing to act the part of a voltaic circuit, in which the hydrogen supplies the place of the electro-positive or oxidizable metal, and the charcoal that of the electro-negative metal or conducting plate. If a plate of platinum, rendered chemically clean,* be introduced into a mixture of pure oxygen and hydrogen, in the proportions to form water, the gases become condensed upon the surface of the plate, and being brought within the sphere of each other's attraction, begin to unite; at first slowly, but during the act of combination heat is developed, and the action proceeds more and more quickly, until at last the plate becomes red hot, and an explosion of the gas ensues (Faraday, *Phil. Trans.*, 1834, 55). By employing the metal in a disintegrated or spongy form, the surface exposed is greater, and the action much more rapid: the metal conducts away but little of the heat which is generated, and soon becomes red hot; whilst in the condition of platinum black (1170) this activity attains its maximum. On throwing a little of this black powder into a mixture of oxygen and hydrogen it immediately becomes incandescent, and the gases combine with a loud report. Platinum may be obtained in a convenient state of fine subdivision for experiments of this nature, by moistening asbestos with a solution of platinic chloride and exposing it to a red heat; the chlorine is expelled, and a film of minutely divided platinum is left upon the surface of each fibre of asbestos.

From its inalterability by ordinary chemical agents, platinum in this finely-divided state has been used to effect various combinations which could not otherwise readily be procured between vaporized and gaseous bodies: For instance, if ammonia be mixed

* This may be effected by holding the plate over the flame of a spirit-lamp and rubbing it, when hot, with a stick of potassic hydrate; the alkali should be maintained in a fused state upon its surface for a second or two, and then washed off completely in distilled water; the plate must now be immersed for a minute in hot oil of vitriol, after which it is freed from adhering acid by immersion for a quarter of an hour in a large bulk of distilled water.

with atmospheric air, and passed over heated spongy platinum, its nitrogen becomes converted into nitric acid, and its hydrogen into water; $NH_3+2O_2=HNO_3+OH_2$: but this transformation cannot be effected by heat alone, as nitric acid is decomposed at a temperature which, under ordinary circumstances, is required to effect the combustion of ammonia. On the other hand, ammonia may be formed from the oxides of nitrogen, by mixing them with hydrogen and passing the gases over platinum sponge gently heated; $N_2O_2+5H_2=2NH_3+2OH_2$. Ammonic nitrate, when heated with platinum black, yields nitric acid, nitrogen, and water, instead of nitrous oxide; thus, $5NH_4NO_3=2HNO_3+4N_2+9OH_2$. A variety of other interesting changes may be effected; for instance, a mixture of hydrocyanic acid and hydrogen when in contact with spongy platinum is partially converted by the aid of a gentle heat into methylamine. In a mixture of nitric oxide and ethylene, ammonic carbonate is produced; and in a mixture of the vapour of alcohol and nitric oxide,—ammonic cyanide and carbonate, ethylene, water and a deposit of carbon are formed. In like manner, sulphurous anhydride may be rapidly converted into sulphuric acid, if it be passed in a moist state, mingled with air, through tubes containing spongy platinum: this method was even proposed as a manufacturing process for obtaining oil of vitriol, but it was abandoned in consequence of a gradual alteration in the platinum, by which it is deprived of this power of effecting the combination. Platinum black produces with the vapours of alcohol in contact with atmospheric air, a series of compounds which are finally converted into acetic acid and water:

$$\overbrace{C_2H_6O}^{\text{Alcohol.}}+O_2=\overbrace{C_2H_4O_2}^{\text{Acetic acid.}}+OH_2.$$

For the success of these experiments, it is necessary that the surface of the platinum be chemically clean, otherwise the combination of the gases does not take place. Faraday considered that these actions are owing to the adhesion of the gases to the surface of the metal, by which the particles of one gas are brought into chemical contact with those of the other. He observed that the admixture of a small quantity of carbonic oxide, or of the vapour of carbonic bisulphide, or of ethylene,* prevented

* Graham finds that in the case of carbonic oxide a gradual oxidation of the carbonic oxide takes place, but that this action is much slower than the oxidation of the hydrogen: the oxidizing influence is wholly concentrated on the carbonic

the platinum from effecting the combination of the oxygen and hydrogen, but did not deprive the metal of its activity, as he ascertained by afterwards plunging it into a mixture of pure oxygen and hydrogen. On the other hand, the addition of sulphuretted or phosphuretted hydrogen to an explosive mixture of oxygen and hydrogen, not only prevents the combination from being produced by the platinum, but it effects such an alteration of the surface of this metal that when it is plunged into a fresh portion of mixed oxygen and hydrogen, no combination of the gases occurs. Hydrochloric acid also rapidly destroys the peculiar properties of finely-divided platinum; according to Döbereiner, the preventive action of this gas depends upon the decomposition of the hydrochloric acid by the oxygen condensed upon the platinum: water is formed, whilst chlorine is liberated, and this chlorine, by converting the platinum superficially into chloride, destroys its power; its activity, however, can be restored by treating it with boiling oil of vitriol. Hydrochloric acid is in this case expelled, and a small quantity of platinous oxide is dissolved; the metal is then to be well washed in distilled water.

(1229) **Other Surface Actions.**—Other finely-divided substances besides platinum possess this property of favouring the combination of oxygen and hydrogen in an inferior degree; even pounded glass, porcelain, charcoal, pumice, and rock crystal, if heated to 320° (608° F.), produce this effect. Finely-divided palladium, rhodium, and iridium also determine the combination of oxygen and hydrogen with explosion at ordinary temperatures. Gold and silver effect the combination of hydrogen with oxygen quietly, at temperatures far below the boiling-point of mercury (Dulong and Thénard). Metals which have a strong chemical attraction for oxygen cannot be used, because they immediately become oxidized upon their surface.

(1230) **Catalysis.**—The remarkable actions produced by the agency of finely-divided platinum have in the foregoing paragraphs been attributed to the force of adhesion, which is supposed to bring the different gaseous bodies within the sphere of mutual action; but they were viewed by Berzelius as arising from a new force, which he termed *catalysis,* in virtue of which, he says, 'Certain bodies exert, by their contact with others, such an influence upon these bodies, that chemical action is excited; compounds are destroyed, or new ones are formed, although the

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oxide, and until this gas is entirely oxidized the hydrogen remains unaltered in the mixture.

substance by which these actions are induced does not take the slightest part in these changes.' This catalytic force, however, is purely imaginary; most of the phenomena which have hitherto been referred to its agency being occasioned by several different causes, which often admit of being distinguished from each other, and which may, as in the case of the action of platinum, be explained by the active operation of other known forces.

Liebig's theory of catalysis is, 'that a body in the act of combination or decomposition enables another body with which it is in contact to enter into the same state. It is evident,' says he, 'that the active state of the atoms of one body has an influence upon the atoms of a body in contact with it, and if these atoms be capable of the same change as the former, they likewise undergo that change, and combinations and decompositions are the consequence. * * * This influence exerted by one compound upon the other, is exactly similar to that which a body in the act of combustion exercises upon a combustible body in its vicinity; with this difference only, that the causes which determine the participation and duration of these conditions are different.'

It has been observed in the case of certain alloys, that the compound is entirely soluble in an acid which may be unable to attack one of the components of the alloy when in a separate form. Platinum, for instance, is not soluble in nitric acid, but if it be alloyed with 10 or 12 parts of silver, the acid dissolves it readily. In like manner, copper is insoluble in dilute sulphuric acid; but an alloy of zinc, nickel, and copper is readily dissolved by this liquid. It is not improbable, however, that electrolytic action plays an important part in this curious phenomenon.

(1231) **Effects of Motion on Chemical Attraction.**—In many cases motion favours the manifestation of cohesion in a remarkable manner: for example, water may be cooled below its freezing-point, and yet retain its liquid form if it be kept perfectly motionless, but on the slightest agitation it solidifies to a mass of ice. Again, if a solution of argentic nitrate be simply mixed with hydrochloric acid, it will long remain milky; but if the nitrate be in excess, and the mixture be briskly shaken for about a minute, the whole of the argentic chloride will collect into dense flocks, which subside rapidly and leave the liquid clear. In a somewhat similar manner motion favours the development of chemical action:—when, for example, a mixture of tartaric acid and potassic nitrate is made, no sign of precipitation will appear for many minutes, if the mixture be left at rest; but if it be stirred briskly with a glass rod, an abundant deposition of crystals

will speedily be produced. A similar effect is often observed with other crystalline precipitates: for instance, the potassic platinic, or ammonic platinic chloride, very often does not appear in dilute solutions until the mixture has been briskly stirred. If the glass rod which is used in stirring the mixture be drawn against the side of the vessel containing the liquid, the track of the rod will be rendered evident by the formation of crystals, which are symmetrically deposited on each side of this line. This effect is particularly manifested when a solution of hydric disodic phosphate is added to dilute neutral magnesic solutions containing ammoniacal salts; the crystalline ammonic magnesic phosphate takes many hours for its complete deposition, unless the liquid be briskly stirred.

Sometimes when the chemical attractions which hold a compound together are feeble, or where the components have a strong tendency to assume the gaseous form, a blow will be sufficient to disturb the equilibrium, and an explosion will follow. In this way the compound known as chloride of nitrogen, which is united by feeble ties, and is composed of bodies which naturally exist in the gaseous state, is sometimes decomposed by the mere fall of a drop of the liquid to the bottom of a jar of the solution in which it is being formed. The ordinary percussion-cap is another instance of the same kind, where the nitrogen in the fulminate suddenly resumes its gaseous state on the application of a blow. In the latter case, and in that of the common lucifer match, it is probable that the heat evolved by the sudden compression attending the blow or the friction, is the cause of these detonations: this explanation certainly also applies to the so-called iodide of nitrogen, which, if dry, explodes when touched even with a feather. Fulminating silver is also decomposed with explosion by causes equally slight.

(1232) **Concurring Attractions.**—Another class of these so-called catalytic phenomena is exemplified in the effect of the admixture of cupric oxide, or manganic dioxide, in aiding the decomposition of potassic chlorate. This chlorate fuses at about 370° (698° F.), and when heated to about 400° (752° F.) it is decomposed with effervescence and a rapid evolution of oxygen: when mixed with about a fourth of its weight of cupric oxide, or of manganic dioxide, the salt begins to be decomposed at a temperature of between 230° and 260° C. (much below its fusing-point); the gas which is given off in this case, however, is always accompanied by a small quantity of chlorine. Other oxides produce a similar effect, but the temperature required varies with

each oxide; thus, the late Dr. Miller found that when the chlorate is mixed with ferric oxide it requires a temperature of about 260° (500° F.); with plumbic oxide a somewhat higher temperature is needed; whilst magnesia and zincic oxide do not aid the decomposition of the salt at all.

This remarkable decomposition appears to admit of an explanation, suggested by Mercer, in elucidation of other somewhat analogous actions. He supposes, although the catalytic body is not found to have experienced any perceptible alteration after the decomposition is complete, that it acts by exerting a feeble chemical attraction upon one of the constituents of the compound. In the case of manganic dioxide and potassic chlorate, the manganic dioxide is a substance which has an attraction for an additional quantity of oxygen, as is evinced by the possibility of forming manganic and permanganic acids from it by further oxidation. This tendency, although it does not rise high enough in the experiment before us to produce either acid, may yet exert sufficient attraction upon the oxygen to facilitate its escape. Indeed, it is not impossible that traces of potassic manganate may be actually formed, and then decomposed; in which case the formation of the small quantity of potash, and the liberation of the chlorine, which always accompanies the oxygen, would be accounted for. A somewhat similar explanation may be applied in the case of the cupric oxide; an unstable sesquioxide of copper appears to exist; cupric oxide, therefore, has a feeble attraction for oxygen, and although that attraction is not adequate to retain the oxygen when separated from the potassic chlorate, it may yet aid in effecting its liberation: ferric oxide is also susceptible in the ferric acid of a higher but unstable stage of oxidation, and the same holds good of plumbic oxide; hence these compounds facilitate the decomposition of the chlorate. There is no proof of the existence of a higher oxide either of magnesium, or of zinc, and accordingly we find that scarcely any effect is produced on heating these oxides with the chlorate. Dr. Miller found also that powdered glass and pure silica were equally inert, probably from the same cause.

A similar result is obtained when a quantity of hydrated cupric oxide, or of manganic dioxide, is thrown into a mixture of bleaching powder and water; on warming the mixture, oxygen is evolved abundantly, and calcic chloride is formed.

Mercer observed that starch, which is ordinarily converted by nitric acid into oxalic acid, is entirely transformed into carbonic anhydride if a salt of manganese be present; $2CO_2$ being

formed, instead of $H_2C_2O_4$. Oxalic acid, also, may be in this manner converted rapidly into carbonic anhydride. If 30 grams of oxalic acid be dissolved in 300 cub. centim. of water, at 82°·2 (180° F.), and 30 c. c. of colourless nitric acid, density 1·30 be added, no decomposition of the oxalic acid occurs; but it immediately commences on adding a small quantity of a solution of manganous nitrate, or any other manganous salt. The manganous oxide, from its tendency to pass into the state of dioxide, tends to deprive the free nitric acid of oxygen, and aids the oxalic acid to decompose this acid; and the oxalic acid having a stronger attraction for oxygen than manganous oxide has, immediately appropriates the oxygen; the united attractions of both being able to accomplish a decomposition which could not have been effected by either separately. An analogous instance of the effect produced by concurring attractions of a more energetic kind is seen in the power possessed by chlorine to decompose silica or alumina when these oxides are mixed with charcoal and ignited (480, 728), although neither chlorine nor charcoal alone is able to produce this effect.

Gaseous ammonia may be passed through heated porcelain tubes at a very high temperature, and it will experience only a partial decomposition; but if the tube be filled with finely-divided metallic copper or iron, the decomposition takes place with facility at a lower temperature. It appears that in this case the metals act by their attraction for nitrogen, which is feeble, and that a nitride of copper or of iron is formed and subsequently decomposed. If iron wire be employed instead of finely-divided iron, it is found to have become superficially altered and brittle (862). Platinum favours the decomposition of ammonia but slightly, and glass scarcely in any appreciable degree.

The decomposition of hydric peroxide (H_2O_2; 354), by contact with many bodies which appear to undergo no chemical alteration during the action, may probably be referred to the same cause. When, for example, finely-divided metallic gold, silver, or platinum, or manganic dioxide, is placed in the liquid peroxide, the latter is decomposed, the oxygen being attracted by the metal, which, however, has not sufficient power to retain it in combination. A singular circumstance, however, has been observed when auric or argentic oxide is substituted for the metal itself; decomposition of the peroxide is produced by the metallic oxide, but the auric or argentic oxide at the same time parts with its oxygen, and is reduced to the metallic state. A similar reaction happens if an acid solution of potassic dichromate be

mixed with the hydric peroxide, the chromic acid losing half its oxygen simultaneously with the hydric peroxide.

Brodie (*Phil. Trans.*, 1850, 759, and 1862, 837) has published the results of a series of experiments, showing that in such decompositions there is a numerical relation between the quantity of the peroxide which is decomposed, and of the metallic oxide which is reduced. These experiments were not confined to hydric peroxide, but were extended to baric and sodic peroxides, which are much more manageable than hydric peroxide. It was found that when the peroxide is mixed with water, and placed in contact with argentic oxide or chloride, that both the compound of barium and that of silver is decomposed; baryta, or baric chloride, being formed, whilst metallic silver and oxygen gas are liberated. When a dilute solution of potassic permanganate is mixed with an acid solution of hydric peroxide, both compounds are decomposed, the permanganate losing an atom of oxygen for each atom of oxygen liberated from the peroxide. A similar decomposition occurs if baric hypochlorite be substituted for potassic permanganate. Brodie connects these experiments with a hypothesis, by which he accounts for the simultaneous liberation of oxygen from the hydric or baric peroxide, and from the argentic oxide or other oxide which undergoes decomposition, and which he applies to chemical decompositions generally: he supposes that the *particles of the same element* may, in certain circumstances, have an attraction for each other:—that, for example, one atom of the oxygen of the baric peroxide may be positive in its relation to the oxygen of the argentic oxide, which he supposes may be negative. In such a case the two particles of oxygen would mutually attract each other, and decomposition of both the oxides would be the result.

$$\overset{-+}{H_2O}\overset{-}{O} + O\overset{-}{Ag_2} = H_2O + \overset{+-}{O}\overset{+-}{O} + Ag_2.$$

Other substances, besides the hydric and the alkaline peroxides, exhibit a similar susceptibility to decomposition by contact with certain bodies. Hydric persulphide, for example, is immediately decomposed by contact with oxides of manganese and silver, and, like hydric peroxide, it is rendered more stable by the addition of acids, whilst its decomposition is facilitated by contact with alkalies (417). The nitrosulphates (450) discovered by Pelouze afford another instance of decomposition effected by a body which undergoes no *apparent* change; but this decomposition is particularly instructive, as it is almost certain that the body which excites the decomposition does suffer a *real* chemical

change. For example, the addition of a solution of cupric sulphate to a solution of ammonic nitrosulphate causes an immediate effervescence, owing to the escape of nitrous oxide. This decomposition appears to be produced thus:—on the addition of cupric sulphate, the nitrosulphate partially exchanges basyls with it: now so long as the nitrosulphuric radicle is in combination with an alkali-metal, the compound has a certain stability, since the alkali-metals appear by their basic energy to preserve the elements *in equilibrio;* but as soon as a salt with a weaker basyl is added, such as cupric sulphate, a portion of cupric nitrosulphate is formed; but the copper being no longer able to maintain this balance, the elements of the compounds arrange themselves in a new order:

$$\underset{\text{Ammonic nitrosulph.}}{(NH_4)_2SO_3N_2O_2} + \underset{\text{Cupric sulph.}}{CuSO_4} = \underset{\text{Ammonic sulph.}}{(NH_4)_2SO_4} + \underset{\text{Cupric nitrosulph.}}{CuSO_3N_2O_2};$$

and the cupric nitrosulphate immediately breaks up into nitrous oxide, and cupric sulphate; $CuSO_3N_2O_2$ becoming $CuSO_4 + N_2O$. Consequently, at the close of the reaction, cupric sulphate is found in the liquid apparently unaltered.

CHAPTER XXVI.

THERMO-CHEMISTRY.

(1233) **General Remarks.**—Of late years so much attention has been given to the relations existing between chemical action and the manifestation of that force we call heat, that it has given rise to what may almost be termed a new branch of chemical science, now generally named thermo-chemistry, for it may be stated generally that no chemical action whatever takes place without development or absorption of heat. From a consideration of the principles of the conservation of energy (330), it will be apparent that, if there be no manifestation of any other force, such as electricity or light, or any change in the physical condition of the substance, as from the solid to the liquid or gaseous state, the amount of heat developed must be the true measure of the chemical action, thus furnishing an accurate means of ascertaining the amount of force put in operation in different cases of chemical action, and consequently of comparing them with one another. At present, however, owing to the many complications introduced by physical changes, only a comparatively few simple reactions have been anything like thoroughly investigated.

In order to compare the results obtained, some standard unit of force must be employed; that which is generally adopted is the amount of heat necessary to raise one gram of water from 4° C. to 5° C. usually called a thermal unit (129,203): thus 100 grams of water raised 1° C., or 200 grams raised 5° C., or 250 grams raised 4° C. might each be supposed to represent a force of 1000 thermal units; this, however, is not strictly true, as more heat is required to raise the temperature of water 1° at high temperatures than at low ones; this is why the unit of heat is fixed at the definite temperature corresponding to the maximum density of water. Many of the effects of heat, however, do not, as yet, admit of measurement.

(1234) **Influence of Temperature on Chemical Attraction.**—Elevation of temperature frequently augments the tendency to combination between bodies which are submitted to its influence:—for example, sulphur or charcoal may be preserved for an indefinite period at ordinary temperatures, in air or in oxygen, without change; but if sulphur be heated to 260° (500° F.), and charcoal to a point a little below a red heat, oxidation commences, and proceeds with such energy that the substance inflames. It not unfrequently happens, however, that a moderate elevation of temperature produces combination, whilst a higher temperature destroys the compound so formed; as, for example, the action of oxygen upon mercury. At ordinary temperatures this metal shows no disposition to combine with oxygen, for it evaporates in air and becomes condensed again in the metallic form; but at a temperature approaching 370° (698° F.), or a little above the boiling-point of the metal, it combines gradually with oxygen and becomes converted into the red oxide, which, at a somewhat higher temperature, is again decomposed into gaseous oxygen and vapour of mercury. Again—baryta at a red heat absorbs a second atom of oxygen, forming baric peroxide, but the second atom of oxygen is expelled by a full white heat, and the compound is reconverted into baryta. A mixture of oxygen and hydrogen may be preserved unchanged at ordinary temperatures, but the introduction of a glass rod heated barely to redness so completely alters their mutual attraction, that sudden combination attended with explosion is the result. This appears to be as pure a case of augmentation of chemical attraction as can be met with, since both the components are thoroughly mixed, and as both are perfect gases, heat cannot in this case act by diminishing cohesion, and so bringing their particles into more intimate contact. Grove, however, has shown that water, this same compound of oxygen

and hydrogen, is resolved into its constituent gases at an intense white heat: by the voltaic ignition of a platinum wire under water, or by the intense heat of a ball of melted platinum raised to whiteness by an alcohol flame animated by a current of oxygen, and then plunged under water, the portion of the latter in immediate contact with the metal is resolved into its elements, and the mixed gases may be collected (*Phil. Trans.*, 1847).

Although elevation of temperature frequently assists combination, yet in many instances it has quite the opposite effect. This is no doubt due to a great extent to the mechanical effect of heat in separating the ultimate atoms of which matter is composed, and from the greater freedom of motion amongst the particles, permitting the atoms to rearrange themselves in new and more stable combinations; the degree of mobility varying with the temperature. For example, olefiant gas at a full red heat loses half its carbon, and is converted into light carburetted hydrogen; and this gas, if subjected to a white heat, deposits the remainder of its carbon, leaving pure hydrogen. Potassic chlorate at a moderate heat is decomposed into perchlorate, and probably into chlorite: the latter salt, however, is immediately resolved into oxygen and potassic chloride; but at a higher temperature the perchlorate in its turn parts with its oxygen, and the more stable potassic chloride is the final result. Numerous other instances of this kind will be presented to the reader when the products of organic chemistry are examined.

A further illustration of this point is afforded by the different products which are furnished by the combustion of the same body at different temperatures. When a jet of cyanogen is burned with a free supply of air, the only products of the combustion are carbonic anhydride and nitrogen; but if a coil of red-hot platinum wire be suspended in a mixture of equal volumes of cyanogen and oxygen, the nitrogen undergoes oxidation as well as the carbon, nitric oxide being formed, as is shown by the appearance of ruddy fumes, owing to the combination of the nitric oxide with free hydrogen. In a similar manner, ether, when burnt freely in air, produces carbonic anhydride and water, $C_4H_{10}O+6O_2$ becoming $4CO_2+5OH_2$; but if a glowing coil of platinum wire be suspended in a mixture of the vapour of ether and atmospheric air, several new products are formed, among which are aldehyde and acetic acid:

$$\overbrace{C_4H_{10}O}^{\text{Ether.}}+O_2=\overbrace{2C_2H_4O}^{\text{Aldehyde.}}+OH_2;\ \text{and}$$

$$\overbrace{C_4H_{10}O}^{\text{Ether.}} + 2O_2 = \overbrace{2C_2H_4O_2}^{\text{Acetic acid.}} + OH_2.$$

(1235) **Dissociation.**—When a rapid current of carbonic anhydride, mixed with steam, is passed through a porcelain tube of 2 inches or $2\frac{1}{2}$ inches (from 5 to 7 cm.) in diameter, which has been filled with clean and previously ignited fragments of porcelain, and the tube is heated intensely in a blast-furnace or forge, it is found that the gas which is left after absorbing the excess of carbonic anhydride by means of potassic hydrate solution consists of an explosive mixture of oxygen, hydrogen, carbonic oxide, and nitrogen: in two experiments, from 25 to 30 cubic centimetres of the mixed gases (from $1\frac{3}{4}$ to 2 cubic inches) were obtained, consisting of

	I.	II.
Oxygen	46·1	46·8
Hydrogen	35·4	31·9
Carbonic oxide	12·0	10·7
Nitrogen	6·5	10·6

Water has here been decomposed into its constituents, part of the liberated hydrogen has exerted a reducing action on the carbonic anhydride, and part of the hydrogen has escaped re-oxidation by its copious dilution with other gases. The presence of nitrogen is due to the entrance of atmospheric air, for however carefully the gases are prepared, it is nearly impossible in an experiment of this kind, which lasts for a couple of hours, to exclude the air perfectly.

A still larger proportion of the explosive mixture is obtained by placing a tube of porous earthenware in the axis of a shorter but wider tube of glazed porcelain, fitting them air-tight with corks, so that a current of any gas may be passed at pleasure through the inner tube, and through the interval between the two tubes. By a suitable arrangement of glass tubes the gases may be collected from either tube separately, and the effects of heating the tubes can be observed upon the issuing gases: for example, if the tube be heated to from 1100° to 1700° (or from about 2000° to 3000° F.) and a current of steam be passed through the inner tube, whilst carbonic anhydride is passed through the outer one, an explosive mixture, similar to that already described, is obtained, but in larger quantity. The hydrogen, at the moment that it is liberated by the effect of heat from its combination with oxygen, at once becomes diffused through the porous tube into the outer one, and there reduces

the carbonic anhydride, whilst the less diffusible oxygen passes on.

In like manner, if a brisk current of pure carbonic anhydride be passed through a porcelain tube filled with fragments of porcelain, and the temperature be raised to 1300° (2372° F.),—after absorbing the carbonic anhydride, a mixture of two volumes of carbonic oxide and one of oxygen, with a little nitrogen, was obtained. To this partial decomposition at elevated temperatures Deville gives the name of *dissociation*. During the occurrence of this phenomenon an absorption of heat takes place exactly corresponding to the force necessary to overcome the chemical attraction of the two elements. The dissociation of compound gases has been carried still further. Carbonic oxide may be resolved into carbon and carbonic anhydride by the following arrangement:—A porcelain tube is placed across a furnace, the temperature of which can be raised very high. In the axis of this tube is supported a thin brass tube of about $\frac{1}{3}$ inch ($8^{mm.}$) in diameter, through which a current of water is kept flowing. Through the outer tube a current of pure carbonic oxide is passed, at a rate of from 4 to 6 litres, or from 250 to 350 cubic inches of the gas per hour. The porcelain tube is gradually raised to bright redness, and on causing the escaping gas to pass through baryta water, a precipitate of baric carbonate is gradually formed, and a layer of black carbon is deposited upon the under surface of the brass tube, where the current of ascending heated gas strikes against the cooled metal. A similar decomposition may be effected by passing a succession of electric sparks through carbonic oxide over mercury, upon which a few drops of concentrated solution of potassic hydrate have been placed to absorb the carbonic anhydride as it is formed.

When instead of carbonic oxide, pure and dry sulphurous anhydride is passed through the porcelain tube, the gas becomes partially resolved into sulphur and sulphuric anhydride. The interior metallic tube in this case was made of copper thickly plated with a voltaic deposit of silver. If this tube be amalgamated, and a current of pure and dry hydrochloric acid be passed through the ignited porcelain tube, heated to at least 1500° (2732° F.), whilst the temperature of the metallic tube is reduced below 50° (122° F.), a deposit of chloride of mercury and chloride of silver is formed in a few hours, and a small quantity of hydrogen may be collected. Decomposition of hydrochloric acid may be effected to a small extent by the continuous discharge of electric sparks for 3 or 4 days through the dry gas; and with sulphurous

anhydride the experiment is easy. Carbonic anhydride is also readily decomposed by the electric spark if a little piece of phosphorus is passed up into the tube to absorb the oxygen as fast as it is liberated.

(1236) **Suspension of Chemical Action by Depression of Temperature.**—As chemical attraction is increased, on the one hand, by elevation of temperature, so, on the other hand, it is diminished by reduction of temperature. Schrötter has shown (*Chemie*, vol. i. p. 129), that, by a sufficient degree of cold, chemical combination may be prevented even between bodies which at the ordinary temperature of the air unite with each other with great energy. Chlorine, for example, combines with phosphorus, or with finely-divided metallic antimony or arsenicum, with such violence that these bodies take fire spontaneously in an atmosphere of the gas; but if the chlorine be cooled down to $-76°{\cdot}1$ ($-105°$ F.), by means of a bath of solid carbonic anhydride and ether, it remains liquid at the ordinary pressure of the air, and it is then quite indifferent to phosphorus, arsenicum, or antimony, provided these substances be cooled to the same temperature before they are added to the liquid chlorine. When the tube in which the mixture is contained is withdrawn from the cold bath, the evaporation of the chlorine occurs with sufficient rapidity to preserve the temperature below the point of combination; but if the free escape of the chlorine be prevented, the temperature rises, and combination occurs with explosive violence. The mutual action of chlorochromic acid and alcohol, of chlorine and ammonia, of iodine or of bromine and phosphorus, and various other actions of a similar nature, may be prevented in the same way.

From these experiments, and from those detailed in the foregoing paragraph, it appears to be most probable that when two bodies have a chemical attraction for each other, there is a certain range of temperature within which they will enter into combination, but if the temperature be raised or depressed beyond a certain limit, their mutual attraction is suspended; and at high temperatures the compound already formed may be destroyed. The temperature most favourable for combination varies with each pair of bodies, and it seems to be probable that there is, for each, a certain temperature at which the maximum of attraction exists, and above and below which it decreases.

(1237) **Attraction between Hydrogen and the Non-metals.**—The attraction between hydrogen and many of the non-metals has been determined with the greatest care by Thomsen of

Copenhagen, and other observers, whose results are of fundamental importance; the constants obtained necessarily entering into a large number of thermal calculations. One of the simplest cases is that of determining the heat developed by the combination of hydrogen and chlorine to form hydrochloric acid. Here both the elements which enter into combination, and also the resulting product, are in the same physical state, for hydrogen is a perfect gas, and chlorine and hydrochloric acid differ so little from that state, as not to interfere with the result. The method employed is to burn a jet of chlorine in an atmosphere of hydrogen contained in a suitable platinum vessel immersed in the water of a calorimeter (202), the hydrogen being renewed as fast as it combines with the chlorine: it is, of course, necessary to take precautions to have both the elementary gases at the same temperature as the water in the calorimeter, and also to pass the hydrochloric acid gas formed through a platinum coil immersed in the water of the calorimeter. The hydrochloric acid issuing from the apparatus is absorbed by water, and its amount determined by the usual methods, so that the weight of chlorine and hydrogen which have combined to form the hydrochloric acid is known. Now, if the heat capacity of the whole apparatus (calorimeter, platinum vessel, &c.) is known, and the temperature has been observed before and after the experiment, we have all the data necessary for calculating the heat developed in the formation of one molecule of hydrochloric acid gas (36·5 grams). This, after making the proper corrections, was found by Thomsen to be 22001 thermal units.

If we determine the amount of heat developed by the combination of oxygen and hydrogen in a manner similar to that employed with hydrochloric acid, we shall find it to be 68357 units for each molecule of water produced (OH_2=18 grams), both the gases and the water formed by their union having a temperature of 18° C. In this case, however, the result is not so simple, since the product obtained is in a different physical state from the elements from which it was formed. The heat developed, therefore, includes not only that resulting from the union of the hydrogen and oxygen to form water, but also that from the liquefaction of the aqueous vapour produced, and the cooling of the resulting water to a temperature of 18° C.

The thermal equivalent, however, cannot always be directly determined, as is the case with the union of hydrogen and iodine to form hydriodic acid, and of nitrogen and hydrogen to form ammonia. Under such circumstances, indirect methods must be

resorted to, depending on the fundamental principle, that *on decomposing a compound into its original elements, the heat absorbed will be equal to that developed by their combination.* In the latter of the two examples mentioned above—namely, ammonia, advantage is taken of this principle to ascertain the amount of heat developed in its formation. When chlorine is passed into dilute aqueous ammonia, taking care to leave the latter in slight excess, decomposition takes place, ammonic chloride is formed, and nitrogen liberated, as shown in the following equation:

$$4NH_3 + 3Cl = 3NH_3.HCl + N.$$

Here one molecule of ammonia is decomposed by 3 atoms of chlorine, with liberation of the nitrogen it contains; the hydrogen combining with the chlorine to form 3 molecules of hydrochloric acid which unite with 3 of ammonia forming 3 of ammonic chloride. The thermic result is here a complicated one consisting of,—1. The heat developed by the union of chlorine and hydrogen in the presence of water; 2. That developed by the combination of the hydrochloric acid formed with ammonia to form ammonic chloride; 3. The absorption of heat produced by the decomposition of the ammonia into its elements, hydrogen and nitrogen; 4. The heat of the absorption of ammonia by water. The heat rendered sensible in the calorimeter by the action of 3 atoms of chlorine ($Cl_3 = 106{\cdot}5$ grams) on 4 molecules of ammonia [$(NH_3)_4 = 68$ grams] in the presence of water is 119613 units:

$$(4NH_3,Aq + 3Cl) = 119613 \text{ units},$$

the union of hydrogen and chlorine in the presence of water is

$$(Cl + H + Aq) = 39315 \text{ units},$$

that of hydrochloric acid and ammonia in presence of water is

$$(NH_3,Aq + HCl,Aq) = 12270 \text{ units};$$

so that the 3 atoms of chlorine combining with 3 of hydrogen, and the union of the resulting 3 molecules of hydrochloric acid with 3 of ammonia to form ammonic chloride will be

$$3(39315 + 12270) = 154755 \text{ thermal units.}$$

The difference between this number and that observed in the calorimeter

$$154755 - 119613 = 35142 \text{ units},$$

represents therefore the heat developed by the union of nitrogen

and hydrogen to form ammonia in the presence of a large amount of water, or

$$(N+H_3+Aq)=35142 \text{ thermal units.}$$

This, however, includes not only the heat produced by the combination of hydrogen and nitrogen to form ammonia, but also the thermal effect of the absorption of ammonia by water, since at the conclusion of the experiment the nitrogen is no longer in solution: this has been found to be $(NH_3+Aq)=8435$. We can now calculate the true thermal equivalent corresponding to the formation of a molecule of ammonia ($NH_3=17$ grams), by the union of its elements—namely, 26707 thermal units

$$(N+H_3+Aq) - (NH_3+Aq) = (N+H_3)$$
$$35142 - 8435 = 26707.$$

The following table represents the results of these determinations as made by Thomsen and by Favre:

	Thomsen.	Favre.
(H+Cl)	22001 units	23783 units
(HCl+Aq)	17314	17479
(NH_3Aq+HClAq) ...	12270	13536
(H+Cl+NH_3Aq) ...	51585	54798
3(H+Cl+NH_3Aq) ...	154755	164394
(4NH_3Aq+3Cl) ...	119613	129720
($N+H_3$+Aq) ...	35142	34674
(NH_3+Aq)	8435	8743
($N+H_3$)	26707	25931

In a somewhat similar manner the thermal effect produced by the union of hydrogen and iodine has been determined by decomposing an aqueous solution of potassic iodide with chlorine, and that of sulphur and hydrogen in sulphuretted hydrogen, by passing that gas into a solution of iodine in hydriodic acid.

H + Cl	22001	thermal units
H + Br	8440	„ „
H + I	−6036	„ „
H_2 + O	68357	„ „
H_2 + S	4512*	„ „
H_3 + N	26707	„ „

* As this number was obtained by thermic observations on the decomposition of hydrogen sulphide by iodine, it applies only to sulphur in that modification in which it is separable from its compounds, and not to the crystalline forms. The number 4950 obtained by Hautefeuille (*Compt. Rend.*, 1869, lxviii. 1554) does not differ materially from that of Thomsen.

In this table of the thermic results of the chemical action between hydrogen and several of the non-metals, as determined by Thomsen, it will be observed that whilst a considerable amount of heat is developed in the union of hydrogen and chlorine, it is comparatively small with bromine, and heat is actually absorbed when hydrogen and iodine combine.

When either hydrochloric, hydrobromic, or hydriodic acid is passed into water, the heat developed is considerably greater than that which is observed in the case of other gases, suggesting the formation of hydrates. This development increases with the amount of water, and also takes place when the concentrated aqueous solution is diluted, just as with sulphuric and nitric acids.

The determination of the thermal effects of the union of carbon and hydrogen is beset with difficulties, arising chiefly from two causes—namely, the complicated nature of most of the compounds of carbon and hydrogen, and our ignorance of the latent heat of carbon vapour, in other words, the amount of force represented by the difference in physical state between the solid carbon and the gaseous hydrogen with which it is combined: to this must be added the complication arising from the difference of heat developed by the allotropic forms of carbon (373), which will be noticed hereafter when considering the attraction of oxygen for the non-metals.

The heat produced by the combustion of the three hydrocarbons, *marsh gas, ethylene,* and *acetylene,* has been carefully determined, with the following results:

Marsh gas	...	CH_4	...	209900 units
Ethylene	...	C_2H_4	...	334800 „
Acetylene	...	C_2H_2	...	310570 „

One molecule of marsh gas in burning consumes 4 atoms of oxygen, and produces 1 molecule of carbonic anhydride and 2 of water, so that the thermal effect observed is the difference between the heat produced by the union of 1 atom of carbon, and 4 of hydrogen with oxygen, and that absorbed in overcoming the force which held together the carbon and hydrogen atoms in the molecule, CH_4. Now the heat developed by an atom of carbon (graphite) in uniting with 2 of oxygen to form carbonic anhydride is 93600, or

$$(C+O_2)=93600 \text{ units};$$

similarly for the 4 atoms of hydrogen in the marsh gas,

$$2(H_2+O)=136714 \text{ units};$$

so that the force uniting the atom of carbon with the four of hydrogen in marsh gas is

$$(C+H_4)=(C+O_2)+2(H_2+O)-(CH_4+O_4)$$
$$20414 = 93600 + 136714 - 209900.$$

It must be noted, however, that the graphite employed in the determination of the thermic value of $(C+O_2)$ is a solid, whilst marsh gas is gaseous.

The results with ethylene will be as follows, employing the same notation:

$$(C_2+H_4)=2(C+O_2)+2(H_2+O)-(C_2H_4+O_6)$$
$$-10886 = 187200 + 136714 - 334800,$$

this result being minus shows that heat is absorbed equivalent to 10886 units by the union of 2 atoms of carbon and 4 of hydrogen to form ethylene.

Again, with acetylene the results are:

$$(C_2+H_2=2(C+O_2)+(H_2+O)-(C_2H_2+O_5$$
$$-55013 = 187200 + 68357 - 310570.$$

An attempt has been made to calculate the latent heat of carbon vapour, or the force necessary to bring carbon out of the passive state in which it is found in graphite, before it can form chemical combinations with the other elements. Since acetylene, C_2H_2, when burnt develops a heat of 310570 units, and H_2 when combining with oxygen to form water 68357 units, it might have been expected that ethylene ($C_2H_4=C_2H_2+H_2$) would give $310570+68357=378927$ thermal units. By experiment, however, it is found to be only 334800; this difference between the theoretical and experimental numbers, 44127 units, has been supposed to represent the attraction which unites the H_2 and C_2H_2 in the compound C_2H_4, or the force by which the two atoms of hydrogen and the acetylene are held together. The theoretical numbers obtained in the combustion of marsh gas are—

For one atom of carbon (graphite) . . .	93600
For four atoms of hydrogen	136714
	230314

From this we must subtract $2\times44127=88254$ units, representing the heat absorbed in overcoming the attraction between C and H_4, supposing always the attraction which unites the C and H_4 to be double that found above for the attraction between C_2H_2 and H_2. This leaves 142060 as the theoretical result of the

combustion of a molecule of marsh gas, CH_4. Experiment, however, shows it to be 209900 units, and the difference between these numbers—namely, 67840 units, has been supposed to represent the latent heat of carbon vapour. There are, however, several assumptions made in this train of reasoning for which at present we have no evidence whatever, especially, that the force which unites the atom of C in marsh gas with the 4 atoms of hydrogen is double that of the difference between the calculated and experimental heats of combustion of ethylene. It seems, however, to be certain that the expenditure of a large amount of force is necessary in order to bring the carbon out of the negative or passive state in which it is in charcoal, diamond, or graphite, before it can form chemical compounds with other elements.

(1238) **Attraction between Oxygen and the Non-Metals.**—The heat of formation of the oxygen acids of the halogens is as follows:

	Chlorine. R=Cl	Bromine. R=Br	Iodine. R=I
$R+O_3+H+Aq$	+23940	+5384	+43537
R_2+O_5+Aq	−20477	−57589	+18717

so that in its affinity for oxygen chlorine stands about midway between bromine and iodine.

Berthelot has found that the absorption of heat in the formation of ozone from oxygen amounts to 29600 units, and as this heat is liberated when oxidation is effected by its means, a satisfactory explanation is offered of its great activity; as, however, the mol. of ozone is O_3, the heat liberated for each atom of oxygen is 9866 units. The cause of the great difference apparent in the energy with which oxidation is effected by various oxidizing mixtures, as potassic dichromate, permanganate, &c., is at once evident, when we consider that the amount of heat evolved by the different reagents varies greatly; and a similar remark applies to reducing agents. This subject is fully treated by Thomsen in *Pog. Ann.*, 1874, cli. 194.

The heat developed by the union of oxygen and carbon varies according to the allotropic form of the element with which the experiment is made. Thus wood charcoal, when completely oxidized to carbonic anhydride, develops heat equivalent to 96960, whilst with graphite, under similar circumstances, it is only 93600 units. Carbonic oxide in burning to carbonic anhydride develops 66800, and therefore graphite in burning to carbonic oxide should produce a heat equivalent to 26800; this is found to be the case. The total amount of heat developed by the burning of a given weight of carbon being the same, whether it is at once

oxidized to its fullest extent, or whether it be first transformed into carbonic oxide, and this gas subsequently burnt to carbonic anhydride.

If we consider the results of the burning of carbon (graphite) in these two stages

$$(C+O) = 26800 \text{ units}$$
$$(CO+O) = 66800 \quad ,,$$

we shall perceive that the amount of heat developed in the first stage—namely, the conversion of graphite into carbonic oxide, is much less than in the second stage, that of the oxidation of carbonic oxide to carbonic anhydride. In every other instance of oxidation, where it takes place by more than one step, the amount of heat developed in the second stage is much less than the first, as might be naturally supposed; the attraction of the element for oxygen being partially satisfied, it would not develop so much heat in combining with a further quantity of oxygen. This apparent anomaly is explained when we consider that the carbon in the first instance has to be brought out of the passive state, previously alluded to when considering the thermic effects of the combustion of the hydrocarbons.

The thermal effects of the union of oxygen with sulphur, selenium, and tellurium, as determined by Thomsen (*Deut. chem. Ges. Ber.*, 1872, v. 1014), are given in the following table:

		Sulphur. R=S	Selenium. R=Se	Tellurium. R=Te
$(R+O_2)$	...	71070 units	57710 units	„ units
$(R+O_2+Aq)$	...	78770 „	56790 „	76300 „
$(R+O_2+Aq)$	...	142400 „	75680 „	100900 „
(RO_2Aq+O)	...	63630 „	18890 „	24600 „

The following table gives the results of formation of the various sulphur acids, both from their elements and from sulphurous anhydride:

$S+O_2+Aq$	=	78770	SO_2+Aq	=	7698
S_2+O_2+Aq	=	75738	SO_2+S+Aq	=	4666
$S+O_3+Aq$	=	142404	SO_2+O+Aq	=	71332
S_2+O_5+Aq	=	211094	$2SO_2+O+Aq$	=	68950
S_3+O_5+Aq	=	208030	$2SO_2+S+O+Aq$	=	65886
S_4+O_5+Aq	=	204965	$2SO_2+S_2+O+Aq$	=	62821
S_5+O_5+Aq	=	201901	$2SO_2+S_3+O+Aq$	=	59757

The thermal equivalent of the oxidation of phosphorus was ascertained by oxidizing finely-divided phosphorus with a solution of iodic acid: the reaction takes place rapidly at the ordinary temperature, and phosphoric and phosphorous acids are produced in equal proportions; and since the thermal effect of the solution

of these acids in water was ascertained, and also the heat developed by the oxidation of both phosphorous and hypophosphorous acids to phosphoric acid, the thermal equivalent of the formation of the three acids can be calculated, and is as follows:

	Crystalline acids.	Solution in water.
H_3+P+O_4	302560	+2690
H_3+P+O_3	227680	— 130
H_3+P+O_2	139950	— 200

In the case of arsenic the formation of the anhydrides is

$$As_2+O_3 = 154590$$
$$As_2+O_5 = 219400$$

The heat of solution of *amorphous* arsenious anhydride can be determined by observing the difference in the thermic effects produced by adding it to a solution of sodic hydrate in the finely-powdered state, and in solution. The result ($As_2O_3+Aq=-7550$) shows that this form of the anhydride dissolves as such in water, and does not take up the elements of water to form an acid (Thomsen, *Deut. chem. Ges. Ber.*, 1874, vii. 996 and 1002).

(1239) **Phenomena of Neutralization.**—The two tables represent some of the results of the neutralization of bases by aqueous sulphuric and hydrochloric acids, and of the neutralization of various acids by an aqueous solution of sodic hydrate so as to form normal sodic salts.

R	Sulphuric acid. ($R+H_2SO_4,Aq$)	Hydrochloric acid. ($R+2HCl,Aq$)
$2LiHO,Aq$	31290 units	27700 units
$2NaHO,Aq$	31380 „	27490 „
$2KHO,Aq$	31290 „	27500 „
$2TlHO,Aq$	31130 „	44340* „
BaH_2O_2,Aq	36900* „	27780 „
SrH_2O_2,Aq	30710 „	27630 „
CaH_2O_2,Aq	31140 „	27900 „
MgH_2O_2	31220 „	27690 „
LaH_2O_2	27470 „	25020 „
CeH_2O_2	26030 „	24160 „
DiH_2O_2	25720 „	23980 „
YH_2O_2	25070 „	23570 „
MnH_2O_2	26480 „	22950 „
NiH_2O_2	26110 „	22580 „
CoH_2O_2	24670 „	21140 „
FeH_2O_2	24920 „	21390 „
CdH_2O_2	23820 „	20290 „
ZnH_2O_2	23410 „	19880 „
CuH_2O_2	18440 „	14910 „
PbH_2O_2	21060* „	14360* „
CuO	18800 „	15270 „
PbO	23500* „	16790* „
Ag_2O	14490 „	42380* „

In the results marked thus * the resulting salt was insoluble, so that the numbers include not only the heat due to neutralization, but that produced by the separation of the solid from the solution.

From an inspection of the first table it will be noticed that the heat developed in the neutralization by acids of certain groups of bases is almost identical: this is particularly the case with lithium, sodium, potassium, and thallium, and also with barium, strontium, calcium, and magnesium; barium is an apparent exception, but the baric sulphate produced is insoluble, and when a correction is made for the heat developed by the separation of the solid compound from solution, the heat due to neutralization falls within the mean for the group: when the alkalies or alkaline earths are dissolved in acids, there is a great dissimilarity in the amount of heat developed, but these discrepancies disappear when they are added to aqueous solution, being in each case about 27500 for hydrochloric acid and 31300 for sulphuric acid. Again, lanthanum, cerium, didymium, and yttrium form a group allied to the strongest bases, but differing from the alkalies and alkaline earths in the difference between the heat of neutralization with sulphuric and hydrochloric acid being much less. It would appear that those bases which are characterized by a close resemblance in their chemical properties, forming well marked groups, arrange themselves in the same manner when the heat developed by their neutralization is considered.

Name of acid.	Formula.	(2NaHO,Aq+2Aq).
Hydrofluoric acid	$2HF$	32540 units
Sulphuric acid	H_2SO_4	31380 „
Selenic acid	H_2SeO_4	30390 „
Sulphurous acid	H_2SO_3	28970 „
Metaphosphoric acid	$2HPO_3$	28750 „
Phosphorous acid	H_3PO_3	28370 „
Oxalic acid	$H_2C_2O_4$	28280 „
Hydrochloric acid	$2HCl$	27480 „
Hydrobromic acid	$2HBr$	27500 „
Hydriodic acid	$2HI$	27350 „
Chloric acid	$2HClO_3$	27520 „
Nitric acid	$2HNO_3$	27360 „
Selenious acid	H_2SeO_3	27020 „
Hydrofluosilicic acid	H_2SiF_6	26620 „
Pyrophosphoric acid	$\frac{1}{2}H_4P_2O_7$	26370 „
Orthophosphoric acid	H_3PO_4	27080 „
Chromic acid	H_2CrO_4	24720 „
Carbonic acid	H_2CO_3	20180 „
Boric acid	$H_2B_2O_4$	20010 „
Hydrosulphuric acid	$2H_2S$	15480 „
Stannic acid	$\frac{1}{2}H_4SnO_4$	4780 „
Silicic acid	$\frac{1}{2}H_4SiO_4$	2710 „

In the neutralization of orthophosphoric acid with soda there is a marked difference in the amount of heat disengaged when the first atom of hydrogen in the acid is replaced by the metal, and in the case of the second and third. The heat developed for the first atom is comparable to that developed in the neutralization of strong acids, whilst for the other two it is very much feebler, resembling carbonic acid or some other weak acid: the three hydrogen atoms in orthophosphoric acid, therefore, have a different value, and the same remark applies to arsenic acid.

(1240) **Double Decomposition.**—It has been ascertained to be a fundamental rule in the double decomposition of two compounds that *the reaction always takes place in such a manner that the greatest amount of heat is developed.* This serves to explain many hitherto incomprehensible reactions; for instance, when hydriodic acid acts on argentic chloride, mutual decomposition takes place, notwithstanding the attraction of chlorine for silver is greater than that between iodine and silver: an examination of the thermal phenomena at once points out the proximate cause: the reaction is

$$HI + AgCl = HCl + AgI;$$

but $(H+I+Aq)+(Ag+Cl)$ and $(H+Cl+Aq)+(Ag+I)$

13171 units + 34800 units and 39315 units + 18651 units.

Hydrogen combining with iodine in the presence of water to form hydriodic acid, develops heat amounting to 13171, and silver when it unites with chlorine 34800; on the other hand, hydrogen and chlorine in the presence of water produce 39315, and silver in combining with iodine 18651. In the first instance the total amount of heat developed is 47971, in the latter 57966, being a difference of 9995, so that when hydriodic acid acts on argentic chloride, hydrochloric acid and argentic iodide are produced, and at the same time heat is developed equivalent to 9995 thermal units.

The formation of hydriodic acid by the action of sulphuretted hydrogen on iodine affords another interesting illustration of this law. As has been already stated, the union of H_2+S to form SH_2 is accompanied by development of heat amounting to 4512 thermal units, whilst in the formation of 2HI the heat absorbed is 12072: it would seem, therefore, that hydriodic acid could not be formed by the action of hydrogen sulphide on iodine, for a force equivalent to 4512 thermal units would be required to separate the H_2 and S, and a force of 12072 to cause the two atoms of hydrogen to unite with two atoms of iodine to form

2HI, or, in other words, in the formation of hydriodic acid by the action of hydrogen sulphide, SH_2, on iodine, I_2, there is no *development* of heat, but, on the contrary, an *absorption* of heat equivalent to 16584 thermal units for the two molecules of hydriodic acid, 2HI. This is strictly in accordance with the observation of Naumann (*Deut. chem. Ges. Ber.*, 1869, iii. 177), that no action takes place between dry iodine and dry hydrogen sulphide, as when the two are dissolved in dry carbonic bisulphide. In the presence of water, however, the case is very different, for the heat developed by the solution of 2HI is 38414 thermal units, which not only supplies the energy equivalent to 16584 thermal units necessary for the formation of hydriodic acid from iodine and sulphuretted hydrogen, but leaves a surplus equivalent to 21830 thermal units, which appears as heat, sensible to the thermometer.

It is evident, from what has been said, that the method of representing reactions generally adopted is not strictly accurate; for the equations of double decomposition merely give the weight of the products before and after the reaction has taken place, but take no account of the energy involved. Thus the equation,

$$H_2SO_4 + Zn = ZnSO_4 + H_2,$$

is a short way of stating that from 98 parts by weight of hydric sulphate and 65 of zinc we may obtain 161 of zincic sulphate and 2 of hydrogen, but it takes no account of the accidents of the reaction, such as the water with which the acid is diluted, the temperature, &c., or of the rearrangement of energy which occurs: this, however, must always be considered if we desire to form a correct idea of any chemical reaction. The above equation may be written

$$A + [H_2SO_4 + \phi(e)] + [Zn + f(e)] = A + [ZnSO_4 + \phi_1(e)] + [H_2 + f_1(e)] + E,$$

where A represents the accidents, such as the water, &c.; $\phi(e)$ the total energy of the molecular weight, H_2SO_4, of sulphuric acid when in solution; $f(e)$, $\phi_1(e)$, $f_1(e)$, the corresponding energy of the zinc, zincic sulphate in solution, and hydrogen. As, however, in almost every reaction heat is either absorbed or developed, it is evident that the sum of the energy of the reagents will not be the same as that of the products, the difference being represented by E, the heat absorbed or developed (where no electrical or similar phenomena occurs). But according to the fundamental law of the conservation of energy, the total energy must be the same before and after the reaction, that is $\phi(e) + f(e) = \phi_1(e) + f_1(e) + E$.

Besides the different relations of heat to chemical action, there are many others in which quantitative determinations of the amount of heat developed have been made, but they are mostly of so complicated a nature that as yet but few and uncertain inferences can be drawn from the results. For instance, in the thermic effects of the solution of a salt containing water of crystallization, we have to consider the change of physical state of the salt from solid to liquid, the total change in volume of the salt and solvent, the effect produced by solution on the water of crystallization of the salt, and probably the partial dissociation of the acid and base in the salt: this, in many instances, has been found to be actually the case; the thermic results show that the ferric salts, for example, are decomposed when they are dissolved in a large quantity of water. Again, the amount of heat developed by the combination of water with anhydrous salts, and the change which takes place when solutions of certain salts are heated, are subjects which offer an extensive field for investigation by this method.

There can be no doubt that when the examinations of thermic phenomena shall have been sufficiently extended, we shall obtain an insight into many problems which are at present inexplicable.

CHAPTER XXVII.

DETERMINATION OF THE COMBINING NUMBERS, AND ATOMIC WEIGHTS OF THE ELEMENTARY BODIES.

(1241) **Aid derived from Analysis in Fixing the Atomic Weight of a Body.**—The determination of the atomic weight of an element involves the performance of analytical operations of great delicacy, and it often presents many very difficult questions for solution. The first object of the chemist is to select some compound of the elementary body under examination, the composition of which is tolerably simple, and which can readily be obtained in a state of purity; and in this compound he determines the proportions of each of its components with the utmost attainable precision. It is of great importance that the operations by which these results are obtained should be as few in number and as simple and manageable as possible. It is not, however, sufficient that three or four different experiments conducted in the same manner should give uniform results: the mode of analysis

adopted should, if possible, be varied so as to avoid any unperceived source of error which depends upon the process employed. It is also desirable to vary the compound upon which the analysis is made. For example, the atomic weight of a metal may, in some instances, be ascertained by fixing the proportion of oxygen which a given weight of the metal absorbs during its conversion into the state of oxide: in other cases the proportion of oxygen and of metal can be determined very exactly by ascertaining the loss of weight which the oxide experiences when a known weight of the pure oxide is heated in a current of hydrogen. It is, however, advisable to check these results, not only by trials upon different quantities of the metal or of the oxide prepared at different times, but also (in order to guard against the occurrence of any unperceived impurity in the substance under experiment) to ascertain if the analysis of the chloride, the sulphide, or some other compound of the metal, gives a similar numerical value for its combining proportion. These results must be reduced by calculation to their weight *in vacuo* (24).*

It is highly probable that many unsuspected sources of error which interfere with the accurate determination of the atomic weight of the elements have still to be discovered; these, however, in most instances, are very slight. For instance, Dumas has recently found that pure silver retains a variable amount of oxygen in solution at the ordinary temperature (*Compt. Rend.*, 1878, lxxxvi. 65), and which it only gives up when heated nearly to redness in a vacuum. This accounts for the minute differences in the atomic weight of silver as determined by different observers, although the experiments were made with every possible care. In all cases the result will be too low, and it is extremely probable that the true atomic weight of silver is 108.

(1242) **Aid derived from Isomorphism, Specific Heat, and Combining Volume of Vapour.**—The determination of the numbers which are assumed to represent the relative atomic weights of the elements, however, does not rest simply upon the knowledge of the proportion in which each element enters into combination with a given amount of oxygen or of any other simple body. When a substance forms but a single combination with oxygen, the simplest hypothesis respecting its composition is, that the com-

* Some idea of the extraordinary care required in researches of this description may be formed by the perusal of the admirable memoirs of Stas, in the Transactions of the Brussels Academy for 1860 and 1865, and that of Crookes on the Atomic Weight of Thallium, in *Phil. Trans.*, 1872.

pound so formed is produced by the union of single atoms of each of its components. Magnesium and zinc, for example, each forms but a single oxide, which is assumed to be a protoxide,—or oxide each molecule of which contains 1 atom of the metal to 1 atom of oxygen. The nitrates formed from such oxides, if represented as consisting of the anhydride and the oxide, $M''O.N_2O_5$, will contain a quantity of the anhydride (N_2O_5), in which the proportion of oxygen is five times that of the base. But it not unfrequently happens that the same metal forms two oxides, in one of which a given weight of oxygen combines with twice as large a proportion of the metal as in the other; for example, 16 parts of oxygen unite with either 63·4 of copper to form the black oxide, or with 126·8 of the metal to form the red oxide; and corresponding salts may be obtained by the reaction of each oxide with acids. In like manner, 16 parts of oxygen form with mercury two basic oxides, one containing 200, the other 400 parts of mercury. The question to be determined then is, which of these numbers is to be regarded as representing the atomic weight of the metal? In cases of this kind, the judgment requires aid from analogy, or from collateral circumstances, such as the isomorphism of the body with some other analogous compound of known composition; the circumstance that the specific heat of the body, when multiplied into its supposed atomic weight, yields the same product as that obtained by multiplying the specific heat of some other element into its admitted atomic number; or the formation of a volume of vapour from the supposed atomic weight which is equal in bulk to the volume of the atom of hydrogen.

Such assistance is afforded in the case of copper by the isomorphism of the compounds of the black oxide of this metal with corresponding compounds of zinc and magnesium. If the oxide of zinc be a protoxide, the black oxide of copper is also a protoxide, and the red oxide must be considered as a suboxide.

Another character of high importance is afforded by the specific heat of the metal. Assuming the oxide of zinc to be a protoxide, the atomic number of the metal is 65·0, and its specific heat is found to be 0·0955; the product of these two numbers is 6·207. The specific heat of copper is 0·0951, and assuming the black oxide to be the protoxide, the atomic weight of the metal is 63·4; the product of these two numbers is 6·029, or nearly the same as in the case of zinc; whereas, if the red oxide were assumed to be the protoxide, it would be double this number. If the numbers given upon pp. 24, 25, Part I., as the atomic weights

of the elements, be multiplied by the specific heat of these bodies in the solid form (Part I., p. 359), the products so obtained will vary but little from the number 6. Exceptions occur in the case of carbon, silicon, and boron, where allotropic modifications interfere. (See also Kopp, *Phil. Trans.*, 1865.)

In the determination of the atomic weights of volatile bodies, assistance may be derived from another character of great importance—viz., the density of their vapour. But the force of this argument will be more fully perceived after the various compounds of organic chemistry, of which so large a proportion are volatile, have been examined.

It is not safe, moreover, to assume in cases in which only one compound exists between an element and oxygen, that such compound is necessarily a protoxide; aluminium is not known to form more than a single oxide, yet chemists do not hesitate to consider this oxide as a sesquioxide, and in this judgment they are guided by analogy: for example, those bodies which are admitted to be protoxides are generally powerful bases, and neutralize the acids very completely. Now alumina does not present this character; its salts have a powerfully acid reaction and taste. But the arguments of most weight against the supposition that alumina is a protoxide are derived from the composition and properties of the oxides of iron. Iron forms two basic oxides: one contains but two-thirds of the proportion of oxygen which is present in the other. The oxide of iron with the smaller proportion of oxygen is a powerful base, and with acids forms salts which are isomorphous with those of magnesia and zincic oxide. It is consequently regarded as a protoxide, and the other oxide is looked upon as a sesquioxide; the basic properties of the latter are much more feeble, and the salts which it forms with acids have, like the salts of aluminium, a powerfully acid reaction. Ferric oxide, moreover, furnishes salts which are isomorphous with those of alumina. An iron alum may be obtained in octahedral crystals, in which the place of the aluminic sulphate is supplied by ferric sulphate: and native ferric oxide is found in forms of the rhombohedral system isomorphous with native alumina in corundum. Hence, if the red oxide of iron be a sesquioxide, alumina must be a sesquioxide also. Moreover, the specific heat of aluminium follows Dulong's law if alumina be a sesquioxide, but not if it be supposed to be a protoxide.

An excellent illustration of the value of isomorphism in these cases is also afforded by the oxides of chromium. Until the publication of Péligot's researches on this metal, only two compounds

of chromium with oxygen were known—viz., the green oxide, and chromic anhydride,—the anhydride containing twice as much oxygen as the oxide. In these two compounds the proportion of oxygen combined with equal weights of chromium was as 1 : 2, or as $1\frac{1}{2}$: 3. But there was little difficulty in deciding that the green oxide must be regarded as a sesquioxide, for the green oxide of chromium was known to be isomorphous with the red oxide of iron, both in its uncombined form, and in the salts which it yields by action upon the same acids. Chromic anhydride would therefore contain 3 atoms of oxygen to 1 atom of the metal. But evidence still more conclusive of the accuracy of this view is afforded by the fact that the chromates are isomorphous with the manganates; now the manganates are known to contain 4 atoms of oxygen, for they are the salts of the acid of a metal which yields a basic oxide with a given weight of manganese containing one-fourth of the oxygen present in manganic acid, H_2MnO_4, and which moreover is isomorphous with the ferrous oxide. Finally, the discovery of another oxide of chromium, with a smaller proportion of oxygen than either of the compounds previously known, fully vindicated the correctness of the foregoing deductions; for the new oxide was found to contain one-third of the proportion of oxygen present in chromic anhydride. It also yields salts isomorphous with the corresponding salts obtained from the protoxide of iron, and the proportion of oxygen which it contains bears the same relation to that present in the green oxide of chromium that the oxygen in the protoxide of iron does to that in the red oxide of iron. Péligot's new oxide therefore was the missing protoxide of chromium.

(1243) **Numerical Data from which the Equivalents and Atomic Weights of the Elements have been Calculated.**

The combining proportions of the elementary substances were first investigated with precision by Berzelius, and the numbers obtained by him, with certain important corrections, are those at present in use. These researches of Berzelius, combined with those of subsequent chemists, particularly of Dumas (*Ann. Chim. Phys.*, 1841, [3], i. 5; 1843, viii. 189; and 1859, lv. 129); of Pelouze (*Compt. Rend.*, 1845, xx. 1047); of De Marignac (*Bibliothèque Univ. de Genève*, xlvi.); of Erdmann and Marchand (*Jour. pr. Chem.*, xxiii., xxvi., xxxi., and xxxiii.); and of Stas (*Trans. Brussels Academy*, 1860, 1865), have furnished most of the following data, from which the numbers given at pp. 24, 25, Part I., have been compiled:—

1. *Aluminium.*—Berzelius found that 100 parts of aluminic sesquisulphate, Al_23SO_4, lost by intense ignition 70·066 of sulphuric anhydride; hence assuming the atomic weight of SO_4 as 96, that of aluminium (hydrogen being = 1) is 27·344. Dumas, by determining the amount of silver required to precipitate a given weight of aluminic chloride, Al_2Cl_6, obtained numbers, from a mean of seven experiments, indicating that the atomic weight of aluminium is 27·488.

2. *Antimony.*—The number 129·03, assigned by Berzelius to antimony, is admitted to have been too high. Schneider, by reducing the native sesquisulphide, Sb_2S_3, to the metallic form, obtained on the average 71·469 per cent. of metal, which would yield as the combining number 120·3. The experiments of Rose on the trichloride, $SbCl_3$, gave 120·69. Dexter, by oxidizing the metal with nitric acid, and converting the residue by ignition into Sb_2O_4, obtained 122·34 as a mean result; and Dumas by experiments upon the trichloride found the quantity of silver required to precipitate this chloride indicated 122·0, as the combining number of the metal, which is that adopted.

3. *Arsenicum.*—Pelouze decomposed a given weight of arsenious chloride, $AsCl_3$, by means of water, and determined the quantity of argentic chloride which it gave when precipitated with argentic nitrate: a mean of three experiments furnished 75 as the atomic weight of arsenicum, a result confirmed by four experiments of Dumas, which gave it as 74·95.

4. *Barium.*—Berzelius found that 100 parts of baric chloride, $BaCl_2$, when dissolved in water, yielded 112·175 of baric sulphate, $BaSO_4$, on the addition of sulphuric acid; and that 100 parts of the chloride when mixed with a solution of argentic nitrate yielded 138·07 of argentic chloride. Pelouze, by precipitation with silver, obtained results almost identical; the number calculated from the results of Berzelius for barium is 136·84; from those of Pelouze, 137·28. De Marignac, from a series of experiments of the same kind, checked by the determination of the barium as sulphate, obtained the number 137·16; and a mean of sixteen experiments conducted in a similar manner by Dumas leads to the number 137·02.

5. *Bismuth.*—100 parts of the metal converted into nitrate and decomposed by heat in a glass vessel, gave 111·275 of sesquioxide, Bi_2O_3, hence the atomic weight of bismuth is 212·86 (Lagerhjelm). Dumas, from a mean of seven experiments upon the quantity of silver required to precipitate the chlorine from a given weight of bismuth chloride, $BiCl_3$, ob-

tained 210·34 as the number for this metal. 210 is the number employed.

6. *Boron.*—According to Berzelius, 100 parts of borax lost 47·1 of water, and yielded 16·31 of soda, leaving for boric anhydride B_2O_3 (by difference) 36·59; and Davy found, by the direct combustion of boron, that 100 parts of boric anhydride contain 32 of boron and 68 of oxygen. This would make the number for boron 10·9. But the methods which were employed are admitted by Berzelius not to be such as to warrant entire confidence in the accuracy of this number; and Deville, from his experiments upon boric trichloride and tribromide, regards 11 as nearer the truth.

7. *Bromine.*—De Marignac found that 3·946 grams of silver, when dissolved in nitric acid, required 4·353 grams of potassic bromide, KBr, for its complete precipitation; and 15·00 of silver converted into nitrate gave 26·11 of argentic bromide: taking the atomic weight of silver at 107·97, a mean of the experiments gives the number for bromine as 79·97; and this result has been verified by Dumas by the decomposition of bromide of silver in a current of chlorine. It may without sensible error be taken as 80.

8. *Cadmium.*—Stromeyer found that 114·352 parts of cadmic oxide, CdO, yielded 14·352 of oxygen; from which the atomic weight of this metal is 111·48. Dumas, as a mean of six experiments upon the quantity of silver required to precipitate the chlorine from a given weight of cadmic chloride, $CdCl_2$, obtained results represented by the number 112·24; but his experiments were not quite so concordant as usual: 112 is the number adopted.

9. *Cæsium.*—The atomic weight of cæsium was ascertained by Bunsen, from determinations of the amount of chlorine and cæsium present in the pure chloride, to be 132·99, whilst Johnson and Allen found 133·03: Godeffroy, who has examined the subject quite recently, makes it 132·557.

10. *Calcium.*—Dumas, by the ignition of 100 parts of Iceland spar, $CaCO_3$, obtained 56 parts of lime, which would make the atomic weight of calcium exactly 40; and the mean of later experiments by the same chemist upon the quantity of silver required to precipitate a given weight of calcic chloride, $CaCl_2$, leads to the number 40·02. Erdmann and Marchand's results would make it 40·06; De Marignac's, by decomposition of a known weight of calcic chloride, 40·21; and those of Berzelius, by the conversion of a known weight of pure lime into sulphate,

would make it 40·26. The number 40 may be safely adopted.

11. *Carbon.*—The determination of the combining proportion of carbon formed the subject of a series of laborious researches by Dumas and Stas. They burned graphite, diamond, and charcoal in a current of pure oxygen with scrupulous care. 1·375 grams of diamond gave 5·041 of carbonic anhydride, CO_2; and the mean of their results, which agreed very closely with each other, entitles us to fix the atomic weight of carbon at 12. Similar experiments by Erdmann and Marchand gave them the number 12·014; and the results obtained by Liebig and Redtenbacher from the combustion of argentic oxalate, $Ag_2C_2O_4$, acetate, racemate, tartrate, correspond to 12·12, which coincides so nearly with the number deduced from those of Dumas, that these chemists themselves have adopted the number which he employs.

12. *Cerium.*—Bunsen carefully determined the atomic weight of this metal by an analysis of the sulphate, both the sulphuric acid and the cerous oxide being estimated. The results of his experiments gave 92 as the atomic weight of cerium, regarding it as a dyad, which was confirmed by Rammelsberg. Bührig has since found that the methods employed for the separation of lanthanum and didymium from the cerium were unsatisfactory, and from careful analyses of the pure oxalate he deduces 94·178 as the atomic weight of cerium considered as a dyad. Hildebrand's researches on the specific heat of the metals cerium, lanthanum, and didymium, however, requires them to be triads, and makes the atomic weights Ce=138, La=139, and Di=144·75. On the same supposition, Bührig's results would give 141·3.

13. *Chlorine.*—Numerous careful experiments have been made with a view to determine the combining proportion of chlorine. De Marignac found that 100 parts of potassic chlorate, $KClO_3$, when decomposed by heat, left 60·839 of potassic chloride, KCl; and 22·032 of pure silver required 15·216 of potassic chloride for its complete precipitation. 14·427 of potassic chloride gave 27·749 of argentic chloride, AgCl. Berzelius calculates from these results that the atomic weight of chlorine is 35·46; and this coincides exactly with the recent elaborate experiments of Stas; a result arrived at also by Penny 30 years ago.

Maumené, by heating argentic chloride in a current of hydrogen, found that 100 parts of silver were united with 32·856

of chlorine. The same chemist obtained from 100 parts of potassic chlorate 60·791 of potassic chloride; and from 100 parts of potassic chloride, he obtained by precipitation 192·75 of argentic chloride. These experiments furnish data from which the atomic weights of potassium and silver may be determined, as well as that of chlorine, in the following manner:

The composition of potassic chlorate is represented by the formula $KClO_3$; when heated it gives off the whole of its 3 atoms of oxygen. The molecule of potassic chloride therefore will be the quantity which is combined with 48 parts (or 3 atoms) of oxygen. Now, taking Maumené's result that 39·209 parts of oxygen are combined in potassic chlorate with 60·791 of potassic chloride, we have—

$$39{\cdot}209 : 48 :: 60{\cdot}791 : x \ (=74{\cdot}4208, \text{ 1 mol. of KCl}).$$

If 100 parts of potassic chloride produce 192·75 of argentic chloride, 1 molecule, or 74·4208, of potassic chloride will furnish 1 molecule of argentic chloride. For—

$$100 : 192{\cdot}75 :: 74{\cdot}4208 : x \ (=143{\cdot}446, \text{ 1 mol. of AgCl});$$

and 132·856 of argentic chloride contain 32·856 of chlorine; consequently (1 molecule of argentic chloride containing 1 atom of chlorine), we find the atomic weight of chlorine as follows:

$$132{\cdot}856 : 32{\cdot}856 :: 143{\cdot}446 : x \ (=35{\cdot}476):$$

but the molecular weight of argentic chloride being	$=143{\cdot}446$
that of silver is found by deducting the at. wt. of Cl	$=35{\cdot}476$
leaving the atomic weight of silver . . .	$=107{\cdot}970$
and the molecular weight of potassic chloride being	$=74{\cdot}4208$
deduct from it the atomic weight of chlorine . .	$=35{\cdot}476$
we obtain the atomic weight of potassium .	$=38{\cdot}9448$

No material error can therefore arise if the atomic weight of

chlorine be taken as	$= 35{\cdot}5$
that of silver	$=108{\cdot}0$
and that of potassium as	$= 39{\cdot}0$

Dumas has also checked these numbers by burning finely-divided silver in a current of perfectly dry chlorine. He thus found that 108 parts of silver combined with 35·505 of chlorine as a mean of two experiments.

14. *Chromium.*—The atomic weight of chromium was determined by Berlin, by converting argentic chromate, Ag_2CrO_4, into

argentic chloride; the number calculated from this result is 52·694; and that deduced from the reduction of the chromic anhydride, CrO_3, to chromic sesquioxide, in the same series of experiments, is 52·54. Péligot's experiments on the acetate would make it between 52 and 53·6, but he considers 52·48 as nearest the truth; the number 52·5 has been adopted.

15. *Cobalt.*—Rothoff found that 269·2 parts of cobalt oxide, CoO, when converted into the chloride, $CoCl_2$, by means of hydrochloric acid and precipitated by means of argentic nitrate, gave 1029·9 of argentic chloride: hence the atomic weight of cobalt is 58·98. The number 59·08 is the mean of five experiments made in a similar way by Dumas. Russell, by reducing the pure oxide, CoO, obtained the number 58·74, and subsequently by dissolving the pure metal in hydrochloric acid and estimating the hydrogen evolved he found 58·76. More recently Winkler has made determinations by weighing the amount of gold precipitated from neutral auric chloride by pure metallic cobalt; this gave 58·992 or 59·0, the number adopted. Lee's determination of the atomic weights from analyses of the crystalline cobaltocyanides of alkaloids of high atomic weight gives as a mean 59·1.

16. *Copper.*—Berzelius obtained from 7·68075 grams of cupric oxide, CuO, which were reduced in a current of hydrogen, 6·13075 of metallic copper; hence the atomic weight of the metal is 63·3. Erdmann and Marchand, by a similar method, obtained numbers which would make it 63·46. More recently Dumas by experiments made on the oxide and on cuprous sulphide obtained results varying from 63·0 to 64·2. Probably 63·4 is nearest the true atomic weight.

17. *Didymium.*—The atomic weight of didymium, regarded as a dyad, as determined from ignition of the oxalate, was found to be 95·14 by Erk; whilst Zschiesche from analyses of the sulphate estimates it at 96·2. This would give 142·5 or 144·3 for the atomic weight, since Hillebrand from determinations of the specific heat of the metal has shown that it is a triad; Clève makes the atomic weight 147·01.

18. *Erbium.*—Bahr and Bunsen in their examination of yttrium and erbium compounds found the atomic weight to be 112·6. Clève's more recent investigations made it 113·7.

19. *Fluorine.*—Berzelius found that 100 parts of fluor-spar, CaF_2, when heated with an excess of sulphuric acid, yielded 175 of calcic sulphate, $CaSO_4$. Louyet, on repeating this experiment, obtained 174·361 parts of calcic sulphate. The atomic

weight of fluorine deduced from this latter result is 19. (*See* p. 261.) These results have been confirmed by Dumas, who made similar experiments upon the fluorides of calcium, potassium, and sodium.

20. *Glucinum.*—Affdejeff found that 100 parts of the chloride of this metal contained 88·42 of chlorine; hence, if the chloride be represented as Gl_2Cl_3, the combining number of the metal will be 6·97; but if the chloride be regarded as GCl_2, as assumed in this work, the atomic weight of the metal is 9·30. This number is confirmed by the results obtained by the same chemist with the sulphate of the metal.

21. *Gold.*—Berzelius, by reducing potassic auric chloride, $KCl.AuCl_3$, in a current of hydrogen, determined the combining number of this metal at 196·66. By an earlier series of experiments he found that 142·9 of metallic mercury precipitated 93·55 of gold from the trichloride, $AuCl_3$; 3 atoms of mercury causing the precipitation of 2 atoms of gold: and assuming the atomic weight of mercury to be 200, this would make the number for gold 196·44.

22. *Hydrogen.*—The atomic weight of hydrogen was determined with great care by Dumas, by the method already described at p. 68. He ascertained, as a mean of nineteen experiments, that 8 parts of oxygen combined with 1·0012 of hydrogen to form water; the lowest quantity which these experiments gave being 0·9984, the highest 1·0045. The quantity of water collected in each of these experiments was considerable, varying from 230 to 1150 grains (15 to 75 grams). Erdmann and Marchand repeated these experiments with similar results. Berzelius and Dulong concluded from researches performed long previously upon a similar principle, though on a smaller scale, that the quantity of hydrogen united with 8 parts of oxygen was 0·9984, which coincides with the lowest number obtained by Dumas. It is obvious that no appreciable error can be committed by assuming hydrogen to possess an atomic weight of 1, that of oxygen being 16, if water be taken as OH_2.

23. *Indium.*—By converting the pure metal into the oxide, In_2O_3, Winkler obtained numbers varying from 113·51 to 113·64, and by decomposing sodic auric chloride with pure indium and weighing the precipitated gold, he found 113·19 and 113·40: the mean of all his experiment gives 113·41.

24. *Iodine.*—De Marignac determined the number for iodine by a process analogous to that which he employed for chlorine. The molecular weight of potassic iodide, KI, he fixed at 165·951;

deducting from this 38·95, Maumené's number for potassium, we obtain 127 as the combining number of iodine. Dumas, from two experiments upon argentic iodide, which he converted into chloride by heating it in a current of dry chlorine, obtained the same result.

25. *Iridium.*—Berzelius deduced the number for iridium from an analysis of the potassio-iridic chloride, $2KCl.IrCl_4$; his results would make it 198·44. The number usually adopted is 198.

26. *Iron.*—Berzelius found that 1·586 grams of pure iron converted first into nitrate, and then into sesquioxide by ignition, gave 2·265 of sesquioxide, Fe_2O_3; and Svanberg and Norlin, by reducing ferric oxide in a current of hydrogen, obtained 25·059 of metallic iron from 35·783 of sesquioxide; making the atomic weight of iron 56·08. Erdmann and Marchand, by the method last named, fixed the atomic weight at 56·002, and Maumené has also arrived at a similar result by dissolving iron in aqua regia, and precipitating the sesquioxide by means of ammonia. Still more recently, Dumas has corroborated the same number by decomposing both the chlorides of iron by means of argentic nitrate—the mean of his four experiments giving 56·14.

27. *Lanthanum.*—The atomic weight of this metal has been determined by Zschiesche by the decomposition of the sulphate. The results of six experiments varied between 89·44 and 91·25, giving a mean of 90·18.

28. *Lead.*—21·9425 grams of plumbic oxide, PbO, were reduced by Berzelius in a current of hydrogen, and gave 20·3695 of metallic lead: from the mean of his fine experiments, the atomic weight of the metal would be 207·14. This result has been confirmed by De Marignac, who obtained, by the precipitation of 5 grams of plumbic chloride, $PbCl_2$, 3·8835 of argentic chloride; similar experiments by Dumas would make the number for lead 207·1, while from those of Stas it would be 206·912.

29. *Lithium.*—The number obtained by Berzelius for this metal, by neutralizing fused lithic carbonate, Li_2CO_3, with sulphuric acid, is probably inaccurate, as this carbonate has subsequently been found to lose a little of its acid when fused. Mallett estimates the atomic weight of lithium at 6·97. Diehl, from an analysis of the carbonate, obtained the number 7·026; and Troost, from the chloride, obtained the number 7·01, as well as by decomposition of the carbonate by means of silica; 7·00 is therefore the number adopted.

30. *Magnesium.*—Berzelius found that 100 parts of magnesia,

dissolved in pure sulphuric acid and ignited, gave 293·985 of magnesic sulphate, $MgSO_4$; hence the atomic weight of magnesium would be 25·3; but this result is probably too high.

Scheerer, by ascertaining the quantity of baric sulphate produced by a given weight of magnesic sulphate, determined the number for magnesium at 24·22. The results of Svanberg and Nordenfelt, by the decomposition of magnesic oxalate, $MgC_2O_4.2OH_2$, by heat, made it 24·7; those by converting a known weight of magnesia into sulphate, gave it as 24·74: whilst those of Marchand and Scheerer, by ignition of the native carbonate, indicated the number 24·04. Scheerer has lately shown that the magnesite employed in these determinations contained minute quantities of calcium, so that this number is probably a little too high. Dumas found extraordinary difficulty in procuring magnesic chloride quite free from magnesia. The mean of eleven experiments upon the precipitation of the chloride, $MgCl_2$, by argentic nitrate gave 24·6 as the combining number of magnesium. The atomic weight usually adopted is 24.

31. *Manganese.*—4·20775 of manganous chloride, $MnCl_2$, gave Berzelius 9·575 of argentic chloride; the atomic weight of the metal, from a mean of two such experiments, is 55·14. Dumas, as a mean of five such experiments conducted in a similar manner, obtained the number 54·96.

32. *Mercury.*—Erdmann and Marchand obtained from 118·3938 grams of mercuric oxide, HgO, 109·6308 of mercury; a mean of five experiments gave 200·2 as the atomic weight of the metal. It may be safely estimated at 200.

33. *Molybdenum.*—Berzelius regarded the number originally given by himself for this metal only as an approximation. Svanberg and Struve, by roasting the molybdous disulphide in air, found that 100 parts of the disulphide, MoS_2, yielded 89·732 of molybdic anhydride, MoO_3; hence, if the atomic weight of sulphur be taken at 32, that of molybdenum will be 92·12. Berlin, from the quantity of molybdic anhydride left by the salt, $(NH_4)_4O_2.5MoO_3.3OH_2$, found the number for the metal to be 91·96. These methods, however, are inaccurate owing to the volatility of molybdic anhydride. Dumas, however, by reducing crystallized molybdic anhydride in a current of hydrogen, found, as a mean of five concordant experiments, 96 as the number for this metal, a result entirely confirmed by Debray's determination by the same method, and also by the formation of argentic molybdate: Meyer, from a careful consideration of Liechte and Kempe's investigation of the chlorides of molybdenum (*Ann.*

Chem. Pharm., 1873, clxix. 344) deduces the number 95·8 as the atomic weight of molybdenum.

34. *Nickel.*—Rothoff converted 188 parts of nickel oxide into chloride, $NiCl_2$, and obtained from it 718·2 of argentic chloride; the number for nickel hence deduced is 59·08: and Dumas, as a mean of five experiments on the same plan, obtained the number 59·02. Russell found it to be 58·738 by reducing the oxide in a current of hydrogen, and 58·7 by measuring the hydrogen evolved on dissolving the pure metal in hydrochloric acid. Winkler, by reducing a neutral solution of sodic auric chloride with the pure metal, and weighing the precipitated gold, obtained the number 59·06. Lee, by analyses of the crystalline double cyanides of nickel with strychnine and brucine, makes the atomic weight of nickel to be only 58·01, or very much below all other observers.

35. *Nitrogen.*—De Marignac, by converting 200 grams of silver into nitrate, $AgNO_3$, obtained 314·894 of the salt; 14·110 of argentic nitrate required for precipitation 6·191 of potassic chloride; 10·339 of silver converted into nitrate required 5·120 of ammonic chloride for complete precipitation: the mean result, as calculated by Berzelius from several experiments performed in this manner, gives 14·004 as the number for nitrogen. Stas, by synthetic experiments upon argentic nitrate, fixed it at 14·044. Anderson, by the decomposition of argentic nitrate by heat, concluded that the atomic weight of nitrogen was 13·95; and Svanberg, from the analysis of plumbic nitrate, $Pb2NO_3$, obtained the same result; the number for nitrogen may therefore be taken as 14.

36. *Osmium.*—The atomic weight of this metal was calculated by Berzelius from the result obtained by heating the potassic osmic chloride, $2KCl.OsCl_4$, in a current of hydrogen, 1·3165 grams of the salt leaving 0·401 gram of KCl and 0·535 gram of osmium: hence the number for osmium will be 198·8, which agrees with the later researches of Dumas: 199 is the number usually employed.

37. *Oxygen.*—The atomic weight of oxygen is the fundamental one from which all others are calculated. Reasons have already been fully given (*see* 'Hydrogen,' p. 963) which lead to the adoption of 16 as the atomic weight of oxygen, if that of hydrogen be taken as 1.

38. *Palladium.*—The number of this metal rests upon the authority of Berzelius, who found, by reducing the chloride of potassium and palladium, $2KCl.PdCl_2$, in a current of hydrogen, that 2·606 grams of the salt gave 0·563 gram of chlorine, 0·851

of palladium, and 1·192 of potassic chloride: hence the atomic weight of palladium is 106·48.

39. *Phosphorus.*—According to Pelouze, a solution of 100 parts of silver in nitric acid is required to precipitate the chlorine from 42·74 of trichloride of phosphorus, PCl_3; the atomic weight of phosphorus, therefore, would be 32·02. Berzelius, from the silver reduced from argentic sulphate by a known weight of phosphorus, estimated the number for phosphorus at 31·36; and Schrötter concludes—from a mean of ten experiments, in which phosphorus was burned in a current of dry air, and thus converted into phosphoric anhydride—that the true atomic weight is 31; a result confirmed by careful experiments upon the trichloride by Dumas, who found it to be 31·03.

40. *Platinum.*—Berzelius found that 6·981 grams of the potassic platinic chloride, $2KCl.PtCl_4$, when reduced in a current of hydrogen, gave 4·957 of a mixture of platinum and potassic chloride; 2·822 of this was platinum: hence the number for platinum is 197·12.

41. *Potassium.*—De Marignac's experiments on potassic chlorate, $KClO_3$, (related when speaking of the atomic weight of chlorine) gave the number for potassium, 39·1; those of Maumené, 38·95; those of Pelouze, 39·14; and those of Stas, 39·137. It may therefore be taken as 39·1.

42. *Rhodium.*—3·146 grams of the potassic rhodic chloride, $KCl.RoCl_3$, when heated in a current of hydrogen, were found by Berzelius to furnish 0·912 gram of rhodium, and 1·304 grams of potassic chloride; whence the atomic weight of the metal should be 104·32.

43. *Rubidium.*—Bunsen's experiments give 85·36 as the atomic weight of this metal, and those of Picard 85·41, whilst Godeffroy's recent experiments make it 85·476. The number employed is 85·47.

44. *Ruthenium.*—Claus found 104·22 to be the atomic weight of ruthenium as deduced from analyses of potassic chlororuthenite.

45. *Selenium.*—100 parts of selenium, when heated in a current of chlorine, according to Berzelius, yield exactly 279 of selenious chloride, $SeCl_4$, which would make the atomic weight 79·32; but the method employed is not perfectly trustworthy. Dumas, by modifying the method of proceeding, obtained as a mean of seven experiments, 79·46.

46. *Silicon.*—Berzelius found that 100 parts of silicon, when oxidized, yielded 208 parts of silica, which, if taken as SiO_2, would give an atomic weight of 29·62; this appears to be too high.

Pelouze states that a solution of 3·685 parts of silver in nitric acid precipitated 1·454 of silicic chloride, $SiCl_4$, whence the number would be 28·48; and Dumas, by a mean of two experiments conducted on the same principle, obtained the number 28·02: further experiments are, however, desirable upon an element of such importance.

47. *Silver.*—The combining number of this metal has been repeatedly determined with very great care, as it forms a fundamental datum in these inquiries. De Marignac, by precipitation of a known weight of silver from its solution in nitric acid, as chloride, AgCl, estimates the equivalent as 107·97; and the experiments of Pelouze and of Maumené agree almost exactly with this result. Dumas has also confirmed this result by burning finely-divided silver in a current of chlorine gas; and the number deduced by Stas, from his experiments, was 107·930. 108 may therefore be taken as the atomic weight of silver.

48. *Sodium.*—Berzelius found that 100 parts of sodic chloride, NaCl, gave by precipitation 244·6 of argentic chloride; the atomic weight of sodium would therefore be 23·17. Pelouze found, as a mean of three experiments, that 100 parts of silver required for precipitation 54·144 of sodic chloride, whence the atomic weight of sodium would be 22·97. Dumas, as a mean of seven experiments of a similar kind, obtained the number 23·01; and Stas found it to be 23·043. It may be taken as 23.

49. *Strontium.*—The number for this metal was also obtained by a similar method, viz., by ascertaining the proportion of silver which a given weight of strontic chloride, $SrCl_2$, requires for precipitation. Stromeyer's experiments give the number 87·34; De Marignac's, 87·54; Pelouze's, 87·68; and the mean of a numerous series of experiments by Dumas, gives 87·53.

50. *Sulphur.*—The atomic weight of sulphur was estimated by Berzelius from the weight of plumbic sulphate formed by oxidizing a known weight of lead with nitric acid, and heating it with an excess of sulphuric acid until the weight ceased to alter. As a mean of three experiments, 100 parts of lead yielded 146·45 of plumbic sulphate, $PbSO_4$; hence the atomic weight of sulphur would be 32·128; this result was confirmed by converting argentic chloride into sulphide in a current of dry sulphuretted hydrogen. Erdmann and Marchand, by distilling cinnabar with copper turnings, obtained from 100 parts of cinnabar, 86·213 of mercury as a mean of two experiments. This would make the atomic weight of sulphur exactly 32—a result which agrees with those of Dumas, who converted a given weight of silver into sulphide, by heating the metal in the vapour of

sulphur. As a mean of five such experiments, he obtained the number 32·02, while Stas found it to be 32·0742.

51. *Tantalum.*—Marignac has made careful determinations of the atomic weight of tantalum by means of the potassic and ammonic fluotantalates, and finds it to be 182. This number agrees perfectly with the vapour density of tantalic pentachloride.

52. *Tellurium.*—1·5715 grams of tellurium when oxidized by nitric acid and heated until the excess of nitric acid was expelled, left a residue of TeO_2, which Berzelius found to weigh 1·9365 grams; hence the number for tellurium would be 128·30. But Dumas, from experiments not hitherto published in detail, gives figures which would make it 129.

53. *Thallium.*—Lamy, by decomposing the sulphate and chloride, obtained results varying from 203·5 to 204·6, and Werther estimates it at from 203·5 to 203·7; but Crookes, who has recently re-determined the atomic weight with the most elaborate precautions by treating a known weight of thallium with nitric acid in an apparatus exhausted of air, from the mean of ten closely agreeing determinations, finds it to be 203·642.

54. *Thorinum.*—Berzelius's experiments gave results which varied between 119·3 and 117·7, and he fixed the atomic weight of thorinum at 118·2. Delafontaine, however, from the mean of a large number of closely agreeing analyses of the sulphate, found it to be 115·7: as, however, thorinum is now regarded as a tetrad analogous to zirconium and tin, this becomes 231·4. Clève's analyses of the dry sulphate make it 233·8, and that of the oxalate 233·97. The atomic weight therefore may be taken as 234.

55. *Tin.*—100 parts of tin, when oxidized by nitric acid and ignited, were found by Berzelius to yield 127·2 parts of stannic oxide, SnO_2; from which the number for tin would be 117·64. Mulder states that he obtained from 100 parts of this metal 127·56 of stannic oxide, which would give the number 116·1. Dumas, on repeating this experiment, obtained the number 118·06 for the metal, and this result was confirmed by experiments on the quantity of silver required for the precipitation of a known weight of stannic chloride, $SnCl_4$. The atomic weight of tin may therefore be taken at 118.

56. *Titanium.*—The number for this metal rests upon the analysis of its tetrachloride. Rose found, as a mean of four experiments, that 100 parts of the tetrachloride, $TiCl_4$, contained 74·46 of chlorine, which would give 48·24 as the atomic weight of titanium. Later experiments by Isidore Pierre, in which 0·8215 gram of $TiCl_4$ furnished 1·84523 grams of AgCl, seem to fix it at 50·34.

57. *Tungsten.*—The number 189·28, calculated from the experiments of Berzelius, was only an approximation. Schneider, on repeating the experiment of reducing tungstic anhydride, WO_3, in a current of hydrogen, found that 100 parts of the anhydride yielded 79·316 of the metal, and on oxidizing metallic tungsten, and reconverting it into tungstic anhydride, he found 79·327 parts of metal furnished 100 of anhydride: the atomic weight of tungsten from the mean of these results would be 184·12. Marchand, by similar experiments, fixed it at 184·1, a result completely confirmed by Dumas; and also by Roscoe's determinations, who obtained a mean of 184·04 by reduction of the trioxide with hydrogen, and by estimation of the chlorine and tungsten in the hexachloride. It may be taken as 184. Persoz, however, has endeavoured to show, although without much probability, that tungstic anhydride consists of TuO_5, not of WO_3, and in such case the atomic weight of tungsten, Tu, would be 153·3. (See *note*, p. 717.)

58. *Uranium.*—Some doubt exists as to the exact combining number of this metal. Wertheim's experiments on the double acetate of sodium and uranium would give 118·48; and Ebelmen's on the oxalate 118·86; but Péligot's estimate, which would make it 120, is usually adopted.

59. *Vanadium.*—The atomic weight of this metal was determined by heating vanadic anhydride, V_2O_5, in a current of hydrogen. It was thus reduced to the sesquioxide. Berzelius found as a mean of four experiments, that 120·927 parts of the anhydride lost thus 20·927 of oxygen. Roscoe found also that as a mean of four experiments 121·22 parts of the anhydride lost by reduction to sesquioxide in a current of hydrogen 21·22 of oxygen, and he calculated the atomic weight of the metal from this at 51·362; while from seventeen experiments on the oxychloride, $VOCl_3$, he obtained 61·276 of chlorine in 100 parts: from these experiments the atomic weight would be 51·05, and as a mean of the two series he adopts 51·3.

60. *Yttrium.*—Bahr and Bunsen, from analyses of the sulphate, YSO_4, obtained 49·30 and 49·24 per cent. YO, giving 61·7 as the atomic weight of yttrium. Delafontaine's results gave 48·23 per cent. YO, whilst Clève, by the same method, made the atomic weight 59·66.

61. *Zinc.*—Favre's experiments on the analysis of zincic oxalate, and on the quantity of hydrogen which a given weight of zinc liberates during its solution in hydrochloric acid, would make the atomic weight of the metal 66·0; and Jacquelain, by the decomposition of the nitrate and of the sulphate of zinc, $ZnSO_4$,

by heat, obtained results corresponding to the number 66·24. The original experiments of Berzelius on this metal lead to the number 64·5. Subsequently, A. Erdmann prepared a pure zincic oxide, mixed it with pure charcoal obtained from sugar, and distilled the zinc in a current of hydrogen; he then oxidized the metal by nitric acid, and converted it into oxide by ignition. The atomic weight of zinc, calculated from a mean of four experiments conducted in this manner, is 65·04. The same number is obtained from the analysis of zincic lactate by Pelouze.

62. *Zirconium.*—As a mean of six experiments, Berzelius found that 100 parts of sulphuric anhydride, SO_3, required 75·853 of zirconia, in order to form the sulphate of the earth. Zirconic fluoride forms with potassic fluoride two compounds: in one the fluorine is combined with zirconium and potassium in equal quantity; in the other the quantity of fluorine combined with zirconium is 3, if that with potassium is 2: hence Berzelius considered that zirconia contains Zr_2O_3, and the combining number of the metal is 67·18, but De Marignac has shown that zirconia is more probably ZrO_2, in which case the number would be 89·5.

(1244) **Table of Combining Numbers.**—We may here sum up the foregoing results, by stating that the following numbers may be taken as representing the atomic weights of the elementary bodies on the hydrogen scale for the purpose of calculating results obtained in the ordinary operations of analyses. They differ but very slightly from the numbers given at pages 24 and 25 of Part I. and at the beginning of this book.

Aluminium	...	27·5	Hydrogen	...	1·0	Rhodium	...	104·3
Antimony	...	122·0	Indium	...	113·4	Rubidium	...	85·5
Arsenicum	...	75·0	Iodine	...	127·0	Ruthenium	...	104·2
Barium	...	137·0	Iridium	...	198·0	Selenium	...	79·1
Bismuth	...	210·0	Iron ...	...	56·0	Silicon	...	28·0
Boron	...	11·0	Lanthanum	...	140·5	Silver	...	108·0
Bromine	...	80·0	Lead...	...	207·0	Sodium	...	23·0
Cadmium	...	112·0	Lithium	...	7·0	Strontium	...	87·6
Cæsium	...	132·5	Magnesium	...	24·0	Sulphur	...	32·0
Calcium	...	40·0	Manganese	...	55·0	Tantalum	...	182·0
Carbon	...	12·0	Mercury	...	200·0	Tellurium	...	129·0
Cerium	...	141·0	Molybdenum	...	96·0	Thallium	...	203·6
Chlorine	...	35·5	Nickel	...	59·0	Thorinum	...	234·0
Chromium	...	52·5	Niobium	...	94·0	Tin ...	...	118·0
Cobalt	...	59·0	Nitrogen	...	14·0	Titanium	...	50·0
Copper	...	63·4	Osmium	...	199·0	Tungsten	...	184·0
Didymium	...	142·5	Oxygen	...	16·0	Uranium	...	120·0
Erbium	...	113·7	Palladium	...	106·5	Vanadium	...	51·3
Fluorine	...	19·0	Phosphorus	...	31·0	Yttrium	...	59·7
Glucinum	...	9·3	Platinum	...	197·1	Zinc ...	...	65·0
Gold ...	...	196·6	Potassium	...	39·1	Zirconium	...	89·5

(1245) **On the Numerical Relations of the Atomic Weights of the Elements.**—Many years ago Prout started the idea that the numbers which represent the combining proportions of the different elementary bodies are multiples by whole numbers of the combining proportion of hydrogen; and he attributed the various cases of apparent departure from this proposition to inaccuracy in the experimental determinations of the combining proportion of the exceptional bodies. Since that period an increased degree of precision has been attained in experiments of this nature, and many of the apparent exceptions to Prout's idea have been removed.

Independently of the importance of accurate determinations of these numbers for the purposes of chemical analysis, and for the tracing out of quantitative relations between the chemical equivalents and certain physical properties, such as the density and specific heat of the simple and compound bodies, the verification or disproof of Prout's hypothesis acquires a high interest from its connexion with the nature of the elementary bodies themselves: for if the combining proportions of all the elements be multiples by whole numbers of the combining proportion of hydrogen, it is not absolutely impossible that the various bodies at present regarded as elementary may consist of a single primordial substance condensed in different degrees in the various so-called elements.

If experiment justifies the hypothesis of Prout, it would be possible that the three following propositions were true:

a. Similar quantities of this one elementary principle might, by variety in the mode of their arrangement, form bodies (at present regarded as elementary) or radicles of equal atomic weight, but endowed with distinct properties.

b. A radicle, intermediate in properties and in its combining number between two other radicles of the same group, might be produced by the union of half a molecule of the two extreme radicles.

c. And, finally, the supposed constitution of these radicles (or bodies at present regarded as simple) might be assimilated to the compound radicles of organic chemistry of known constitution. There would be, however, this important distinction between the radicles of mineral chemistry and those of organic origin; viz., that the radicles of inorganic chemistry possess a stability indefinitely greater than those of the organic creation—a stability, indeed, of such an order that the present resources of analytical chemistry are insufficient to effect their decomposition.

The probability, on the other hand, of such views would obviously be negatived if the elements exhibited no such multiple relation in their equivalents.

Certain remarkable relations which exist between many of these numbers have been pointed out by various chemists. The whole subject of atomic weights was a few years ago submitted to a careful revision by Dumas (*Ann. Chim. Phys.*, 1859, [3], lv. 129). As the result of his investigations and calculations, Dumas concludes that, in a modified sense, Prout's law is true; and he considers that the elementary bodies, the atomic weights of which he regards as accurately known, may be arranged in three groups, or rather two groups, if the duplication of the atomic weights adopted in this work be followed—viz.:

1. Bodies which are represented by multiples of a whole number of the atomic weight of hydrogen.

2. Multiples by the number 0·5 of that of hydrogen.

1. Bodies which are multiples by a whole number of the atomic weight of hydrogen:

Hydrogen	1	Arsenicum	75
Lithium	7	Bromine	80
Boron	11	Molybdenum	96
Carbon	12	Silver	108
Nitrogen	14	Cadmium	112
Oxygen	16	Tin	118
Fluorine	19	Antimony	122
Sodium	23	Iodine	127
Magnesium	24	Tellurium	129
Silicon	28	Cæsium	133
Phosphorus	31	Barium	137
Sulphur	32	Cerium	141
Calcium	40	Tantalum	182
Manganese	55	Tungsten	184
Iron	56	Osmium	199
Cobalt	59	Mercury	200
Nickel	59	Lead	207
Zinc	65	Bismuth	210

2. Multiples by 0·5 of the atomic weight of hydrogen.

Aluminium	27·5	Selenium	79·5
Chlorine	35·5	Zirconium	89·5
Chromium	52·5	Palladium	106·5

The relations exhibited between the numbers of many of these bodies which are chemically allied are often very remarkable:

1. It has been observed that, in several instances where two elements are in close chemical relation to each other, they have

atomic weights which are identical; this happens, for example, with the following pairs of bodies:

Cobalt and Nickel	59
Rhodium and Ruthenium	104·2

2. In other cases, the ratio of the atomic weights is as 1 to 2; for instance:

Oxygen	= 16	Sulphur	= 32
Aluminium	= 27·5	Manganese	= 55

3. It has also been stated that, where three elements belong to the same natural group, the atomic weight of the intermediate element is frequently equal to the mean of those of the two extremes. This is true in the case of

$$\begin{array}{l} \text{Lithium} = 7 \\ \text{Sodium} = 23 \\ \text{Potassium} = 39{\cdot}1 \end{array} \quad ; \quad \frac{7 + 39{\cdot}1}{2} = 23{\cdot}05;$$

the number for sodium being the arithmetic mean of those for lithium and potassium: but this is the only case in which this relation is rigidly in accordance with the experimental numbers. Several groups agree very nearly with such a supposition, but the divergence is, notwithstanding, too great to admit of being attributed to errors of experiment. For example:

$$\begin{array}{l} \text{Calcium} = 40 \\ \text{Strontium} = 87{\cdot}6 \\ \text{Barium} = 137{\cdot}0 \end{array} \quad ; \quad \frac{40 + 137}{2} = 88{\cdot}5$$

$$\begin{array}{l} \text{Sulphur} = 32 \\ \text{Selenium} = 79{\cdot}5 \\ \text{Tellurium} = 129{\cdot}0 \end{array} \quad ; \quad \frac{32 + 129}{2} = 80{\cdot}5$$

In both these groups, the difference between the experimental and the calculated number of the intermediate elements amounts to 1·0; and it is probable that this difference is physically true.

In cases like the lithium and calcium groups, it has been suggested, both by Pettenkofer and by Dumas, that the relation between the different members of the group may be analogous to that observed in bodies of organic origin which belong to the same homologous series. The reader who is desirous of pursuing this speculation will find it ably and clearly discussed by Dumas in his paper already cited (*Ann. Chim. Phys.*, 1859, [3], lv. 164).

(1246) **Relations between the Atomic Weights; Periodic Law of Newlands and Mendelejeff.**—If the elements are arranged in the order of their atomic weights from H=1 to U=240, it will be found that, with the exception of certain gaps, the relations between their properties, their quantivalence, and their atomic weights, takes the form of a periodic function. This

periodic law was first pointed out by Newlands in 1864 (*Chem. News*, x. 58 and 94), who called it the law of octaves, as he observed that when arranged in this way, every eighth element, starting from a given one, was a kind of repetition of the first, like the eighth note in the musical octave. Thus, if the fourteen elements whose atomic weights be between 7 (lithium) and 35·5 (chlorine) be arranged in two groups of 7,

1	2	3	4	5	6	7
Li 7	G 9·4	B 11	C 12	N 14	O = 16	F = 19
Na 23	Mg 24	Al 27·3	Si 28	P 31	S = 32	Cl = 35·5

it will readily be seen that the 1st and the 8th members of the series, lithium and sodium, are closely allied in properties; and the same may be said of the 2nd and 9th (G and Mg), the 3rd and 10th (B and Al), the 4th and 11th (C and Si), and so on.

The deductions capable of being made when this arrangement of the elements is adopted was subsequently discussed by Odling, and the subject has since been greatly extended and developed by Mendelejeff (*Ann. Chem. Pharm.*, 1870, *Sup.*, viii. 132).

1	2	3	4	5	6	7	8	9	10	11	12
H 1	Li 7	Na 23	K 39	Cu 63	Rb 85	Ag 108	Cs 133	...	Au 199	...	RCl
	G = 9·4	Mg 24	Ca 40	Zn 65	Sr 87	Cd 112	Ba 137	...	Hg 200	...	RCl_2
	B 11	Al 27	...	Ga 70	Y 88	In 113	Di 138	Er 178	Tl 204	...	RCl_3
	C 12	Si 28	Ti 48	...	Zr 90	Sn 118	Ce 140	La 180	Pb 207	Th 231	RCl_4
	N 14	P 31	V 51	As 75	Nb 94	Sb 122	...	Ta 182	Bi 210	...	RCl_5
	O 16	S 32	Cr 52	Se 78	Mo 96	Te ?125	...	W 184	...	U 240	RCl_6
	F 19	Cl 35·5	Mn 55	Br 80	...	I 127	...	...	...	...	RCl_7
			Fe 56 Co 59 Ni 59		Ru 104 Rh 104 Pd 106			Os ?195 Ir ?197 Pt 198			

An examination of this table shows that the known elements, with 9 exceptions, may be arranged in 11 groups; of these H stands by itself in the first group, but the other 10 groups contain 7 elements, each with occasional gaps. All the metals in the first horizontal line combine with one equivalent of chlorine, and are univalent, forming compounds of the general formula, RCl; those in the second line are dyads, or bivalent; those in the

third line are triads, and so on. With regard to those elements which occur in the sixth line, chromium is a hexad, as it forms a hexafluoride, CrF_6, and uranium forms a trioxide, UO_3. Sulphur is usually a dyad, but its chlorine compounds show that it is capable of acting as a tetrad, and in some of its organic compounds it is undoubtedly a hexad; and the formula for sulphuric acid, $S^{vi}(O''_2)(OH)_2$, in which sulphur is represented as hexad, is more consistent with the stability of the compound than (HO)−O−S″−O−(OH), where it is represented as a dyad, inasmuch as compounds in which dyad elements are linked together in a row are for the most part very unstable. In the seventh line, manganese appears to be a heptad, and this agrees with what is known of the permanganates; and in the perchlorates, $Cl^{vii}(O'')_3(OR)$, and periodates, from their analogy with the permanganates, chlorine and iodine may be supposed to be heptads. Again, in most cases, the corresponding members of an even and uneven series differ from one another much more than those of two even or two uneven series; for instance, rubidium (series 6) is closely allied to cæsium (series 8), but differs widely from silver (series 7). Calcium, strontium, and barium also form a natural group (even series), as do magnesium, zinc, and cadmium (uneven series), and sulphur, selenium, and tellurium. There is a very strongly marked difference in properties between the last member of an even series and the first member of the preceding or succeeding uneven series—between chlorine and potassium, for instance, or iodine and cæsium or rubidium.

Now, between the last members of an even series and the following uneven series, each including seven elements, and not irregularly dispersed amongst the individual members of the series, there occur every one of those elements which from their properties are excluded from these series; they form three groups of three each—

Fe 56	Ru 104	Os 193*
Ni 59	Rh 104	Ir 195*
Co 59	Pd 106	Pt 197

The metals of these three groups are all greyish-white and difficult of fusion, they possess the power of occluding hydrogen

* The numbers given for osmium and iridium are not those usually accepted, but it must be borne in mind that the experiments hitherto made to ascertain the atomic weight of these metals cannot be looked upon as having accurately decided what they are.

and other gases to a high degree, especially palladium, platinum, iron, and nickel. Their higher oxides are easily reduced to lower oxides of decided basic character, and they all form double cyanides with the alkali-metals.

It will be observed in the table (p. 975) that the atomic weight of some of the elements is different from that given in the body of the work; uranium, for instance, is made 240 instead of 120. Mendelejeff points out that the latter number coming between Ag = 108 and I = 127 would give it a place in the system which does not correspond with its properties, and would also derange the order of the succeeding elements; moreover it has no analogy with the metals of the iron group, from which it is distinguished both by its high density, 18·4, and by the oxide possessing feebler basic properties. If 240 is taken as the atomic weight, it becomes a hexad, which is quite in accordance with the close analogy between its peroxide and those of chromium, molybdenum, and tungsten, CrO_3, MoO_3, and WO_3.

In the case of tellurium, the periodic law requires that the atomic weight should be between that of Sb = 122 and I = 127, and as Ag − Cu = 45; Cd − Zn = 47; Sb − As = 47; I − Br = 47; Cs − Rb = 48; Ba − Sr = 50; it may be supposed that Te − Se will be about 47; this would make 125 the atomic weight of tellurium. The actual determinations of the atomic weight (129) do not agree with this result, but it is not improbable, considering the difficulty of purifying tellurium, that this number may be modified by future investigations.

Many other curious relations between the elements besides those mentioned have been pointed out by Newlands in a paper 'On relations among the atomic weights of the elements when arranged in their natural order' (*Chem. News*, 1875, xxxi. 21).

(1247) **Experiments of Stas on Atomic Weights.**—Stas arrives at a conclusion respecting Prout's hypothesis entirely opposite to that of Dumas, previously mentioned. He has published two memoirs (*Trans. Brussels Acad. Sci.*, 1860, 1865) containing the results of a long and most laborious series of researches, which it appears almost impossible to surpass in precision. In the last memoir (p. 23), he gives the following numbers for some of the most important elements (O = 16):

Oxygen ...	...	...	16·000
Silver ...	...	...	107·930
Lead ...	...	...	206·912
Potassium	...	...	39·137
Sodium ...	...	...	23·043
Lithium	...	...	7·022
Chlorine	...	...	35·457
Bromine	...	...	79·952
Iodine ...	...	...	126·850
Nitrogen	...	...	14·044
Sulphur	...	...	32·074

The numbers for lead and sulphur are founded upon experiments in the earlier memoir.

These results have been obtained in each case by several different processes; and the differences between the various numbers thus arrived at for the same body are in all cases much smaller than the difference between the mean result and the whole number required by Prout's law. These numbers were obtained by operating with balances of unusual delicacy, and upon quantities much larger than is customary in researches of this kind—the quantities amounting in some cases to nearly a pound weight of the materials.

The numbers thus obtained do not differ from those of Dumas, or indeed from those in general use, sufficiently to affect any calculations of analysis founded upon them; but from the variety of methods employed, and the extraordinary degree of care and precision with which the experiments were made, the results are of the highest value in relation to the hypothesis of Prout.

Stas concludes his first memoir with these words:

'So long as we adhere to the results of experiment for the establishment of the laws by which matter is governed, we ought to consider the law of Prout as a pure illusion, and should regard the indecomposible substances of our globe as distinct bodies, having no simple relations between their atomic weights. The undeniable analogy in properties which is observed in certain of the elements must be sought for in other causes than those derivable from the relations in weight of their acting masses.'*

In his second memoir, he further says, at p. 23: 'To resume and to conclude, I have inquired whether the law of chemical proportion is a *limited* law, or a law of rigorous accuracy. I think that I have proved that it is the expression of a mathematical relation. I think also that I have shown that the atomic weight of the same body determined by the aid of different elements, and by methods independent of each other—a weight which *ought* to be identical in each case, *is* so in reality within the limits of accuracy which it is possible by our present methods of investigation to attain.'

* It has been shown, however (p. 954), that unsuspected sources of error may affect even the most carefully conducted experiments, which materially affects any argument founded upon the supposition that they are absolutely accurate.

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